Xenobiotics in freshwater streams of Hesse, Germany

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Dekan: Prof. Dr. Gerhard Brey

Gutachter: Prof. Dr. Wilhelm Püttmann
Prof. Dr. Jörg Oehlmann

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Contents

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Zusammenfassung (Summary)

Im Rahmen des Projektes INTAFERE (Integrierte Analyse von mobilen, organischen Fremdstoffen in Fließgewässern) wurden organische Spurenverunreinigungen in Fließgewässern des Hessischen Rieds mit dem Ziel untersucht, deren Vorkommen, die zeitliche und räumliche Varianz im Fließgewässer sowie mögliche Eintragsquellen und Senken zu beschreiben. Organische Mikroverunreinigungen wurden in den letzen Jahren zunehmend in den Fokus wissenschaftlicher Untersuchungen gerückt (Boyd et al., 2003; Daughton und Ternes, 1999; Dsikowitzky et al., 2004a; Kolpin et al., 2002; Poiger et al., 2003), da immer neue und immer mehr Chemikalien auf den Markt kommen, die in die Umwelt gelangen können und die wegen geringer Kenntnisse über deren öko- und humantoxikologische Wirkung ein potentielles Risiko für Mensch und Umwelt darstellen. In diesem Zusammenhang wird häufig von „neuen" Schadstoffen in Anlehnung an den englischen Sprachgebrauch verbreiteten Begriff der „emerging contaminants" gesprochen. Diese Substanzen sind i.d.R. durch hohe Produktionsmengen bzw. ubiquitäres Vorkommen in Konsumgütern, eine geringe biologische Abbaubarkeit, sowie eine mittlere bis hohe Polarität gekennzeichnet. Entsprechend ihrer Anwendung lassen sich diese Substanzen überwiegend den folgenden Stoffgruppen zuordnen: Flammschutzmittel, Weichmacher, Körperpflegemittel, Arzneimittel, Antioxidantien, Pflanzenschutzmittel und Detergentien. Für die vorliegende Arbeit wurden repräsentative Vertreter dieser Stoffgruppen ausgewählt und in den Fließgewässern des Hessischen Rieds untersucht. Dazu gehörten u.a. die Organophosphate Tributylphosphat (TBP), Tris(2-butoxyethyl)phosphat (TBEP), Tris(2-chlorethyl)phosphat (TCEP), Tris(1-chlorisopropyl)phosphat (TCPP) und Tris(1,3-dichlor-2-propyl)phosphat (TDCPP), welche vorwiegend als Flammschutzmittel und Weichmacher eingesetzt werden und daher ein breites Anwendungsspektrum in Kosumgütern aufweisen. Allein in Westeuropa wurden Ende der 1990er Jahre etwa 360.000 t/a Flammschutzmittel verbraucht, davon entfielen ca. 72.000 t/a auf phosphororganische Flammschutzmittel (Metzger und Möhle, 2001).

Weiterhin wurden die synthetischen Moschusverbindungen 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-g-2-benzopyran (HHCB) und 7-Acetyl- 1,1,3,4,4,6 hexamethyl-tetralin (AHTN) analysiert, die als Duftstoffe in Produkten der Kosmetikindustrie sowie in Detergentien und Reinigungsprodukten zur Anwendung kommen. Mit einem Verbrauch von 1.427 t/a bzw. 434 t/a im Jahr 2000 machen HHCB und AHTN ca. 95 % der in der EU konsumierten synthetischen Moschusverbindungen aus. Im

Fokus der Untersuchung standen des weiteren die Alkylphenole 4-tert.-Octylphenol (OP) und das technische Isomerengemisch 4-Nonylphenol (NP), welche endokrin wirksame Ausgangs- und Umwandlungsprodukte der Octylphenolphenolethoxylate (OPEOs) bzw. der Nonylphenolphenolethoxylate (NPEOs) sind, die wiederum vorwiegend als Industriereiniger aber auch für die Emulsionspolymerisation sowie als Hilfsmittel in der Leder- und Textilindustrie eingesetzt werden. In Deutschland wurden im Jahr 2001 ca. 37.000 t/a NPEOs und 2.000 t/a OPEOs produziert (Leisewitz et al., 2001b). Als eine weitere wichtige Industriechemikalie mit Produktionsmengen von weltweit etwa 2,8 Millionen t/a (Bisphenol A Global Industry Group, 2004) wurde Bisphenol A (BPA) in den Fließgewässern des Hessischen Rieds analysiert. BPA wird für die Herstellung von Kunststoffen verwendet, insbesondere für die Produktion von Epoxydharzen und Polykarbonaten und ist ebenfalls endokrin wirksam. Neben den Organophosphaten, den synthetischen Moschusverbindungen und den genannten endokrinen Disruptoren wurden des weiteren das Insektenrepellent N,N-Diethyl-m-toluamid (DEET) sowie das Pflanzenschutzmittel Terbutryn als Zielsubstanzen ausgewählt. Terbutryn ist ein Herbizid aus der Triazingruppe und wirkt hemmend auf die Photosynthese. Es ist damit nahezu universell einsetzbar und kommt vorwiegend beim Anbau von Wintergerste, Mais, Hirse, Kartoffeln und Erbsen zur Unkrautbekämpfung zum Einsatz. Weiterhin kann Terbutryn auch zur Bekämpfung von Algen in Fischteichen, Speicherbecken oder kleineren Fließgewässern angewandt werden. In Deutschland wurde die Anwendungsgenehmigung für Terbutryn aufgrund der Verordnung Nr. 2076/2002 der Europäischen Kommission zum 25. Juli 2003 zurückgenommen, wobei Restbestände bis Ende 2003 aufgebraucht werden durften. Das Inkrafttreten des Anwendungsverbot von Terbutryn als Pflanzenschutzmittel in Deutschland fiel damit in den Untersuchungszeitraum (September 2003 bis September 2006). Hingegen unterliegt das Insektenrepellent DEET in Deutschland keinerlei Regulierung und wird in Fließgewässern und Kläranlagen immer wieder nachgewiesen (Dsikowitzky et al., 2004, Knepper et al., 1996). Bis in die 1990er Jahre war DEET der Wirkstoff in dem von Bayer produzierten Insektenschutzmittel Autan®, bis es wegen gesundheitlicher Bedenken insbesondere bei Schwangeren durch Bayrepel (1-Piperidincarboxylsäure-2-(2-hydroxyethyl)-1-methylpropylester) ersetzt wurde. In zahlreichen Produkten anderer Hersteller (z.B. Antibrumm® von Togal) ist DEET jedoch nach wie vor enthalten.

Untersuchungsgegenstand waren vier Bachsysteme im Hessischen Ried, welches durch einen hohen Grad an anthropogener Belastung (hohe Bevölkerungsdichte, Industrie- und

Gewerbestandort, intensive landwirtschaftliche Nutzung) gekennzeichnet ist. Von besonderer Relevanz ist weiterhin, dass das Untersuchungsgebiet auch ein bedeutendes Trinkwassereinzugsgebiet für das Rhein-Main-Gebiet (insbesondere Frankfurt am Main) darstellt. Die Überwachung der Wasserqualität der Oberflächengewässer (als mögliche Quellen für Grundwasserkontaminationen) ist daher von eminenter Bedeutung. Das Untersuchungsgebiet wird von vier Bachsystemen durchzogen, die alle von Ost nach West fließend in den Rhein entwässern. Von Nord nach Süd sind das wie folgt: Schwarzbach - Landgraben, Modau - Sandbach, Winkelbach – Lauter und Weschnitz Die Fließgewässer sind erheblich anthropogen beeinflusst: einerseits durch Abwassereinleitungen und andererseits durch z.T. starke Verbauung bzw. Veränderung des Fließquerschnitts sowie durch landwirtschaftliche Aktivitäten. Im Einzugsgebiet der vier Bachsysteme liegen insgesamt 28 Kläranlagen, deren Ausbaugröße zusammengerechnet ca. 1,18 Mio. Einwohnergleichwerten (EWG) entspricht. Das Schwarzbach – Landgrabensystem ist mit ca. 477.600 EWG im Mündungsbereich am stärksten von diesem Abwassereintrag betroffen, der Winkelbach mit 95.750 EWG am geringsten. In dieser niederschlagsarmen Region (550 bis 600 mm/a) kann der Abwasseranteil bei Niedrigwasser bis nahezu 100 Prozent betragen. Letzteres ist neben der Wirkung auf die aquatischen Lebewesen insbesondere deshalb bedenklich, da die Fließgewässer Modau, Winkelbach und Weschnitz überwiegend infiltrierenden Charakter zeigen (RP Darmstadt, 1999) und daher mit organischen Spurenstoffen belastetes Oberflächenwasser ins Grundwasser gelangen kann.

Die Probenahme an den Fließgewässern des Hessischen Rieds erfolgte an insgesamt 26 Messstellen. An den Messtellen wurden jeweils 2,5 Liter als Wasserprobe entnommen. Die Beprobung erfolgte im Zeitraum von September 2003 bis September 2006 jeweils vierteljährlich. Vor Ort wurden außerdem während der Probenahme die Parameter Leitfähigkeit, Abfluss, pH - Wert und die Wassertemperatur gemessen. Zur Klärung relevanter Eintragspfade wurden im Juni und September 2005 zusätzlich fünf Kläranlagenabläufe, welche in die Fließgewässer des Hessischen Rieds entwässern, beprobt. Nach Eingang der Proben im Labor wurden die Proben zunächst gefiltert, anschließend mit Hilfe der Festphasenextraktion angereichert und mittels gekoppelter Gaschromatographie – Massenspektrometrie (GC-MS) analysiert. Die Quantifizierung erfolgte über einen internen Standard, wobei die Nachweisgrenzen für die Zielsubstanzen bei dieser Methode im Bereich von 3,6 ng/l bis 18,4 ng/l lagen. Die Wiederfindungsraten lagen zwischen 74 % und 104 %.

Die Ergebnisse der Untersuchung zeigten, dass die Fließgewässer des Hessischen Rieds erheblich mit organischen Spurenstoffen belastet sind. So konnten die Organophosphate mit Nachweishäufigkeiten von ca. 90 % detektiert werden und kommen nahezu ubiquitär in den Fließgewässern des Untersuchungsgebietes vor. TCPP ist mit 502 ng/l und einer Nachweishäufigkeit von 99 % das mit der höchsten Konzentration vertretene Organophosphat in den untersuchten Fließgewässern. Die mittleren Konzentrationen der anderen analysierten Organophosphate liegen mit 276 ng/l (TBP), 183 ng/l (TBEP), 118 ng/l (TCEP) und 117 ng/l (TDCPP) jeweils deutlich darunter. Die ermittelten Maximalkonzentrationen waren um eine Größenordnung höher und betrugen 3.889 ng/l (TBP), 1.773 ng/l (TBEP), 2.019 ng/l (TCEP), 2.914 ng/l (TCPP) sowie 1.284 ng/l (TDCPP). Vor dem Hintergrund der hohen Varianz der Konzentrationen während des Untersuchungszeitraums waren keine saisonalen Unterschiede feststellbar.
Insgesamt liegen die ermittelten Konzentrationen der Organophosphate im Bereich früherer Studien an deutschen Fließgewässern (Andresen et al., 2004; ARGE-ELBE, 2000; Dsikowitzky et al., 2004b; Fooken, 1997). Im Vergleich mit früheren Messungen aus hessischen Fließgewässern des Untersuchungsgebietes (Fooken, 2000) sind insbesondere die Konzentrationen von TCPP deutlich erhöht im Vergleich zu den Jahren 1991 – 2000. Im Falle von TBP lagen die gemessenen Konzentrationen im Hessischen Ried bereits in den Jahren 1999 – 2001 geringfügig über denen anderer Regionen Deutschlands (Leisewitz et al., 2001b). Dieser Trend scheint sich fortzusetzen und ist mit dem relativ hohen Abwasseranteil in den Fließgewässern des Hessischen Rieds erklärbar.

Neben der hohen zeitlichen Varianz der Konzentrationen der Organophosphate sind auch erhebliche räumliche Konzentrationsschwankungen erkennbar. So waren die im stark abwasserbeeinflussten Schwarzbach-System beobachteten Konzentrationen der Organophosphate deutlich höher als im Winkelbach. Bei den chlorierten Organophosphaten wurde eine positive Korrelation der ermittelten Frachten einer Probestelle mit der dort abgeleiteten Abwassermenge anhand der Einwohnergleichwerte festgestellt. Damit konnten die Kläranlagen als ein wesentlicher Eintragspfad für die chlorierten Organophosphate identifiziert werden. Daneben weisen lokal begrenzt auftretende, hohe Konzentrationen insbesondere an wenig abwasserbeeinflussten Messstellen auf die Existenz von diffusen und diskontinuierlichen Quellen (z.B. Oberflächenabfluss) hin. Die mittleren Frachten der Organophosphate nahmen von der Quelle zur Mündung hin zu. Dies deutet darauf hin, dass der Eintrag der Substanzen in die untersuchten Fließgewässer den Abbau in den Gewässern

übersteigt. Insgesamt waren die beobachteten Frachten geringer als in anderen Studien (Dsikowitzky et al., 2004b), was auf die geringeren Abfluss zurückgeführt werden kann.

Die synthetischen Moschusverbindungen HHCB und AHTN konnten ebenfalls sehr häufig (Nachweishäufigkeit 90 %) in den Fließgewässern in Konzentrationen von durchschnittlich 141 ng/l bzw. 46 ng/l nachgewiesen werden. Die Maximalkonzentrationen lagen bei 678 ng/l (HHCB) sowie 299 ng/l (AHTN). Die Werte liegen damit im Bereich der Konzentrationen aus früheren Messkampagnen des Hessischen Landesamtes für Umwelt und Geologie (HLUG) an hessischen Fließgewässern (Fooken, 2000). Die gemessenen HHCB und AHTN Konzentrationen waren stark miteinander korreliert und lagen in einem stabilen Verhältnis von HHCB : AHTN = 3 vor. Dieses Verhältnis entspricht in etwa der Relation der jährlich in der EU verbrauchten Mengen an HHCB und AHTN von 1.427 t/a und 434 t/a (IFRA, 2002). Im Gegensatz zu den Organophosphaten zeigten die synthetischen Moschusstoffe einen deutlichen saisonalen Trend. So waren die ermittelten Konzentrationen und Frachten im Sommer deutlich geringer als in den Winter-, Herbst- oder Frühlingsmonaten. In den Sommermonaten lagen die durchschnittlichen Wassertemperaturen der Fließgewässer bei etwa 20°C (zum Vergleich: 12°C im Frühling und im Herbst, 4°C im Winter), so dass von einer stärkeren Verdampfung der leichter flüchtigen Stoffe aus dem Wasser ausgegangen werden kann. Des weiteren sind HHCB und AHTN photolytisch abbaubar (Buerge et al., 2003), so dass auch die erhöhte Sonneneinstrahlung in den Sommermonaten zu der geringeren Belastung der Fließgewässer mit synthetischen Moschusverbindungen beigetragen haben kann. Die Analyse der Abwasserbelastung an den jeweiligen Probenahmestellen anhand der Einwohnergleichwerte zeigte, dass die Kläranlagen als Haupteintragspfade für die synthetischen Moschusverbindungen fungieren. Die höchsten Konzentrationen wurden demzufolge in den Fließgewässern mit höherer Abwasserlast gemessen. So wies der stark abwasserbeeinflusste Schwarzbach – Landgraben die höchsten Konzentrationen der Moschusverbindungen auf, während im deutlich geringer belasteten Winkelbach die geringsten Konzentrationen gemessen wurden. Mit zunehmender Entfernung der Probenahmestellen vom Ort der Einleitung durch eine Kläranlage konnte zudem eine Abnahme der Konzentration beobachtet werden. Ebenso wie bei den Organophosphaten nahmen die Frachten der synthetischen Moschusverbindungen in den Fließgewässern jeweils zur Mündung hin zu.

Die endokrin wirksamen Substanzen BPA, NP sowie OP konnten in den Fließgewässern mit Konzentrationen von <20 ng/l bis 1.927 ng/l, <10 ng/l bis 770 ng/l und <10 ng/l bis 420 ng/l

detektiert werden. Während OP weit verbreitet war und in etwa 2/3 aller Proben vorkam, konnten NP und BPA dagegen nur in 56 % bzw. in 13 % der Fälle nachgewiesen werden. Im Falle von NP wurden die höchsten Konzentrationen im September 2003 gemessen. Die „predicted no effect concentration“ (PNEC) von 0,33 µg/l wurde zu diesem Probenahmezeitpunkt an 16 (von 23) Probestellen überschritten, zu allen späteren Zeitpunkten jedoch nicht mehr. Von September 2003 bis Juni 2004 nahmen die gemessenen NP - Konzentrationen kontinuierlich ab. Im Oktober und Dezember 2004 nahmen die Konzentrationen und die Anzahl der Detektionen wieder leicht zu, allerdings lagen die Werte um eine Größenordnung niedriger als noch im September 2003. Im April und Juni 2005 konnte in keiner Probe NP nachgewiesen werden. Dagegen war NP in den anschließenden Probenahmen von September 2005 bis September 2006 wieder häufiger in den Fließgewässern nachweisbar – allerdings lagen die Konzentrationen mit Monatsmittelwerten zwischen 18 ng/l (September 2006) und 46 ng/l (Dezember 2005) ebenfalls deutlich unter denen von September 2003 (426 ng/l). Analog zu den NP – Konzentrationen haben auch die NP – Frachten in den Fließgewässern deutlich abgenommen, so dass von einem tatsächlichen Rückgang der NP – Einträge in die Gewässer und nicht etwa von einem Verdünnungseffekt auszugehen ist. Als Grund für die Abnahme der NP – Konzentrationen und Frachten wird vielmehr die Umsetzung der EU-Richtlinie 2003/53/EG, welche die Nutzung von NP stark einschränkt, angenommen. Die Auswertung der zusätzlich im Sommer 2005 beprobten Kläranlagenabläufe zeigte des weiteren, dass Kläranlagen nicht die einzige Quelle für NP in den Fließgewässern sein können, da NP nur in einem der beprobten Abläufe nachgewiesen werden konnte, in einer Konzentration knapp oberhalb der Nachweisgrenze von 8 ng/l. Zum gleichen Zeitpunkt war NP jedoch in den Fließgewässern in erheblich höheren Konzentrationen nachweisbar. Als mögliche Quellen hierfür können die Rücklösung von NP aus dem Sediment und/oder ein Eintrag mit Oberflächenabfluss in Betracht gezogen werden.

Im Gegensatz zu NP sind die Konzentrationen und Frachten von OP – welches ein ähnliches Anwendungsfeld wie NP besitzt, dessen Nutzung jedoch nicht durch regulatorische Maßnahmen eingeschränkt wurde - im Untersuchungszeitraum nicht oder nur leicht zurückgegangen. Die höchsten Konzentrationen wurden im September 2003 mit durchschnittlich 97 ng/l gemessen, die geringsten im April 2005 mit insgesamt nur drei Messwerten oberhalb der Nachweisgrenze von 10 ng/l. Letzteres kann auf einen Verdünnungseffekt durch hohe Niederschläge und die Schneeschmelze zurückgeführt werden. Im Mittel lagen die OP - Konzentrationen in den Fließgewässern des Hessischen Rieds bei 30 ng/l. In 9 % der Fälle überstiegen die gemessenen OP - Konzentrationen den in einer

Studie des Bundesumweltamtes (Rüdel et al., 2001) vorgeschlagenen PNEC von 100 ng/l. Mit Ausnahme von September 2005 wurde dieser Wert in jeweils mindestens einer Wasserprobe pro Probenahmekampagne überschritten. Im Allgemeinen lagen die gemessenen Konzentrationen im Bereich der aus anderen europäischen Fließgewässern bekannten Werte (Bolz et al., 2001; Scheffknecht, 2005; Stachel et al., 2003). OP wurde in der Vergangenheit häufig in Kläranlagenabläufen nachgewiesen (Ahel et al., 2000; Bolz et al., 2001; Espejo et al., 2002; Höhne und Püttmann, 2006a). In Proben der Kläranlagenabläufe aus dem Untersuchungsgebiet wurde OP in Konzentrationen von bis zu 333 ng/l gefunden. Dabei erfolgt der Eintrag aus den Kläranlagen im Untersuchungsgebiet offenbar eher diskontinuierlich, da OP nur in vier von acht Proben der Kläranlagenabläufe nachweisbar war. BPA konnte vergleichsweise selten in den Fließgewässern nachgewiesen werden, dafür jedoch in z.T. sehr hohen Konzentrationen von bis zu 1.924 ng/l. Bei diesen Konzentrationen sind schädliche Wirkungen auf aquatische Lebewesen nicht auszuschließen. Der PNEC von 1.600 ng/l wurde in zwei Fällen und zwar jeweils im September 2003 überschritten, jedoch wurden auch zu späteren Zeitpunkten (z.B. im Oktober 2004) noch Konzentrationen im Mikrogrammbereich gemessen. Die ermittelten BPA-Konzentrationen lassen jedoch keinerlei saisonale oder räumliche Muster erkennen. Eine mögliche Ursache hierfür könnte in der guten biologischen Abbaubarkeit (Dorn, 1987) von BPA begründet liegen, so dass eventuell vorhandene BPA Einträge in die Fließgewässer relativ schnell abgebaut werden und durch die punktuelle Probenahme nur schlecht abgebildet werden. Des weiteren kann BPA an Schwebstoff bzw. an Sedimentbestandteile adsorbieren (Stachel et al., 2003) und damit aus der Wasserphase eliminiert werden. Auch in den beprobten Kläranlagenabläufen konnte BPA nicht nachgewiesen werden. Es wird daher vermutet, dass die gelegentlichen BPA - Funde in den Fließgewässern eventuell von sporadischen Durchbrüchen in Kläranlagen resultieren, jedoch relativ zügig im Gewässer abgebaut werden.

Das Pflanzenschutzmittel Terbutryn wurde insbesondere in der Weschnitz und der Modau in sehr hohen Konzentrationen nachgewiesen. Die Spitzenkonzentrationen in Weschnitz und Modau betrugen 5.600 ng/l bzw. 3.067 ng/l, bei mittleren Terbutrynkonzentrationen von 536 ng/l und 583 ng/l. Auch in Schwarzbach und Winkelbach ist Terbutryn häufig vorzufinden, wenn auch in deutlich geringeren Konzentrationen von durchschnittlich 63 ng/l bzw. 28 ng/l. Die Terbutrynkonzentrationen und Frachten zeigen einen deutlichen saisonalen Trend mit jeweils höheren Werten in den Sommer- und Herbstmonaten. Entsprechend der Richtlinie 91/414/EWG des Europäischen Rates und der Verordnung (EG) 2076/2002 der

Europäischen Kommission wurde die Lizenz für terbutrynhaltige Pflanzenschutzmittel zum 25.7.2003 zurückgezogen, daher ist die Anwendung als Pflanzenschutzmittel in Deutschland seit spätestens 13.12.2003 verboten. Ein Rückgang der Terbutrynkonzentrationen bzw. der Frachten in den Fließgewässern des Hessischen Rieds konnte jedoch über den gesamten Probenahmezeitraum nicht beobachtet werden. Trotz der inzwischen verbotenen Verwendung in Pflanzenschutzmitteln darf Terbutryn weiterhin als Wirkstoff in Dachfarben eingesetzt werden (Menge, 2005). Daher kann nicht genau geklärt werden, aus welcher Anwendung das Herbizid in die Fließgewässer gelangt. Durch die Beprobung einzelner Kläranlagenabläufe im Hessischen Ried konnten die Kläranlagen als möglicher Eintragspfad für Terbutryn identifiziert werden. Dabei konnten allerdings große Unterschiede hinsichtlich der eingeleiteten Mengen an Terbutryn festgestellt werden. So wiesen drei der untersuchten Kläranlagen nur jeweils geringe Konzentrationen im Ablauf im Bereich von 30 ng/l bis 90 ng/l auf. Dagegen konnten in den Abläufen der Kläranlagen des Abwasserverbandes Bergstrasse nahe Weinheim und der Kläranlage Darmstadt/ Eberstadt Terbutrynkonzentrationen von 3.530 ng/l bzw. 330 ng/l nachgewiesen werden. Insbesondere die Kläranlage Weinheim trägt demnach in erheblichem Maße zur Terbutrynbelastung der Weschnitz bei. Frühere Untersuchungen zeigten, dass Pflanzenschutzmittel in erheblichen Maßen über die Kanalisation in die Kläranlagen eingetragen werden können (Seel et al., 1996). Hauptursache hierfür ist das Reinigen der Arbeitsgeräte sowie Spritzverluste entlang von an die Kanalisation angeschlossenen Wirtschaftswegen.

Das Insektenrepellent DEET konnte mit einer Nachweishäufigkeit von 70 % und Konzentrationen von < 8 ng/l bis 1.292 ng/l n den Fließgewässern des Hessischen Rieds nachgewiesen werden. DEET gelangt vorwiegend über die Kläranlagenabläufe in die Fließgewässer (Knepper et al., 1996). Wegen seiner hohen Wirksamkeit wird DEET insbesondere bei Reisen in die Tropen empfohlen und kommt nach wie vor in zahlreichen Produkten der Insektenabwehr zur Anwendung (z.B. Feldtosan®, Antibrumm®, MosiGuard®, DEET Anti-Insekt Lotion 50 Care Plus®). In den Fließgewässern des Hessischen Rieds zeigten die DEET – Konzentrationen ein saisonales Muster mit deutlich höheren Konzentrationen im Sommer (150 ng/l), was mit der Hauptanwendungszeit als Insektenrepellent korrespondiert. In den Herbst-, Winter- und Frühlingsmonaten konnte DEET mit durchschnittlich 60 ng/l, 40 ng/l und 50 ng/l in den Fließgewässern des Hessischen Rieds nachgewiesen werden. Knepper et al. (1996) beobachteten in Main und Rhein ein vergleichbares saisonales Muster und konnten das Vorkommen von DEET in den Kläranlagen

außerhalb der Insektensaison zunächst nicht erklären. In einer späteren Untersuchung führt Knepper (2004a) diese Beobachtung auf das Waschen von Kleidung nach der Rückkehr von Reisen aus wärmeren Regionen zurück. Des weiteren zeigte Knepper (2004a), dass die Reinigungsleistung der Kläranlagen stark abhängig von der Zulaufkonzentration ist und eine relevante Elimination von DEET erst bei Zulaufkonzentrationen oberhalb von 300 ng/l erfolgte, welche nur in den Sommermonaten erreicht wurde. In den Fließgewässern des Hessischen Rieds konnte die Abhängigkeit der gemessenen DEET – Konzentrationen von der eingetragenen Abwassermenge anhand der Korrelation (R = 0.5) zwischen der Anzahl der angeschlossenen Einwohner an einer Probestelle und den dort im Mittel bestimmten DEET - Konzentrationen nachgewiesen werden. Entsprechend wurden höhere Konzentrationen im Schwarzbach mit durchschnittlich 245 ng/l gefunden, wohingegen Weschnitz, Winkelbach und Modau mit 64 ng/l, 70 ng/l und 82 ng/l deutlich geringere Belastungen mit DEET aufwiesen. Knepper fand eine deutliche Abnahme der DEET – Konzentrationen nachdem DEET Ende der 1990er Jahre durch Bayrepel ersetzt worden war. Die im Hessischen Ried im Zeitraum September 2003 bis September 2006 bestimmten DEET – Konzentrationen von 60 ng/l zeigten keine weitere Abnahme über diesen Zeitraum, sondern sind vergleichbar mit denen, die Knepper (2004b) Ende der 1990er Jahre in Main und Rhein fanden.

Die untersuchten organischen Spurenverunreinigungen sind in unterschiedlichem Maße von regulatorischen Maßnahmen betroffen. So wird beispielsweise NP durch die EU Richtlinie 2003/53/EG seit dem 1.1.2005 europaweit stark reglementiert, während die Anwendung von Terbutryn bisher nur in Pflanzenschutzmitteln und auch nicht in allen EU – Mitgliedstaaten untersagt ist. Des weiteren gibt es Substanzen, welche durch freiwillige Selbstverpflichtungen einzelner oder mehrerer Produzenten eingeschränkt wurden. Dazu gehören z.B. TCEP und DEET, welche in den 1990er Jahren durch entsprechende Ersatzstoffe (TCPP und Bayrepel®) ersetzt wurden. Die Effizienz dieser freiwilligen Selbstverpflichtungen ist jedoch umstritten (Anton et al., 2004; Arimura et al., 2007; Blackman, 2007; Jimenez, 2007; Khanna, 2001; Morgenstern und Pizer, 2007). So zeigten beispielsweise die Monitoringergebnisse dieser Studie, dass TCEP und DEET weiterhin sehr häufig in den Fließgewässern des Hessischen Rieds vorkommen, wenn auch in Konzentrationen, die deutlich unter dem Niveau der 1990er Jahre liegen. Auch im Falle von NP gab es in den 1990er Jahren eine Selbstverpflichtung der Industrie zur Reduktion von NP. Einen relevanten Rückgang der NP Konzentrationen in den Fließgewässern auf ein akzeptables Niveau, d.h. unterhalb des PNEC, ist allerdings erst seit der Umsetzung der EU Richtlinie im Jahr 2005 zu beobachten. Insofern können freiwillige

Selbstverpflichtungen im Rahmen von umweltpolitischen Maßnahmen zwar durchaus positive Effekte auf die Umwelt haben, sie sind in ihrer Wirksamkeit jedoch offenbar begrenzt.

Short summary

The present study was elaborated within the scope of the INTAFERE (Integrated Analysis of Mobile Organic Foreign Substances in Rivers) project which investigates the occurrence of xenobiotics in small freshwater streams with particular consideration of social impact factors. The aim of this study is to investigate the seasonal and spatial variance of organic micropollutants in small fresh water streams and to identify possible sources and sinks.

Therefore, four small freshwater river systems in Hesse, Germany have been investigated with respect to common organic pollutants such as the organophosphates tri-n-butyl phosphate (TBP), tris(2-butoxyethyl)phosphate (TBEP), tris(2-chloroethyl)phosphate (TCEP), tris(1-chloro-2-propyl)phosphate (TCPP), and tris(1,3-dichloro-2-propyl)phosphate (TDCPP), the synthetic musk fragrances 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta-[γ]-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN), the endocrine disruptors bisphenol A (BPA), 4-*tert*-octylphenol (OP), the technical isomer mixture of 4-nonylphenol (NP), the herbicide terbutryn [2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine], and the insect repellent N,N-diethyl-m-toluamide (DEET). Water samples were collected in the time span from September 2003 to September 2006 at 26 sampling locations with 13 sampling campaigns at intervals of 2 to 4 months, leading to an overall sample amount of 330 samples. The samples were extracted with solid phase extraction (SPE) and analyzed by coupled gas chromatography-mass spectrometry (GC-MS). For quantification purposes, the internal standard method was used yielding detection limits for the target compounds between 3.6 ng/l and 18.4 ng/l. Recovery rates were between 74 % and 104 %.

The results of the study showed an ubiquitous occurrence of organic pollutants in the fresh water streams of the study area. The organophosphates have been detected in 90 % of the water samples with mean concentrations of 502 ng/l (TCPP), 276 ng/l (TBP), 183 ng/l (TBEP), 118 ng/l (TCEP), and 117 ng/l (TDCPP). Sewage treatment plant (STP) effluents were identified as the dominating source for the chlorinated organophosphates as well as for the synthetic musk fragrances and the insect repellent DEET in the river systems. Consequently, the highest concentrations were observed in the Schwarzbach river system characterized by the highest proportion of waste water compared to the other river systems. The mean concentration levels of the synthetic musk fragrances HHCB and ATHN were 141 ng/l and 46 ng/l, respectively and 124 ng/l in the case of DEET. The synthetic musk fragrances showed a clear seasonal trend with significantly lower concentrations in summer

compared to winter seasons, which is ascribed to stronger photodegradation and volatization during the summer. In contrast, mean DEET concentrations and loads were significantly higher in summer (150 ng/l) than in autumn, winter, and spring (60 ng/l, 40 ng/l and 50 ng/l, respectively), parallel with the main insect season.

The concentrations of the endocrine disruptors BPA, NP, and OP in the river water samples ranged from <20 ng/l to 1927 ng/l, <10 ng/l to 770 ng/l, and <10 ng/l to 420 ng/l, respectively. Whereas OP was present in about two-thirds of the samples, NP and BPA could only be detected in 56 % and 13 % of the water samples respectively. BPA levels exceeded in two samples the predicted no-effect concentration (PNEC) of 1,600 ng/l for water organisms. In the case of NP, the highest concentrations and loads were found in September 2003 and decreased significantly since then. In contrast, concentrations and loads of OP, which serves in a similar application field, remained nearly constant during the sampling period. The decrease of NP can be attributed to the implementation of the European Directive 2003/53/EG, which restricted the use of nonylphenols and nonylphenol ethoxylates since January 2005. However, at the end of the sampling period in September 2006, NP was still detected at mean concentrations of 18 ng/l in the river waters of the sampling area. Furthermore, the absence of NP in several samples from associated STP effluents indicates that the STPs cannot be the only sources for NP found in the river water.

The herbicide terbutryn was present in the rivers during the whole sampling period from September 2003 to September 2006, despite a ban on its use as a herbicide since January 2004. Terbutryn levels ranged from < 4 ng/l to 5,600 ng/l, showing a clear spatial pattern with high terbutryn concentrations in the Weschnitz (536 ng/l) and Modau (583 ng/l) river systems and significantly lower terbutryn levels in Schwarzbach (63 ng/l) and Winkelbach (28 ng/l). Results from the analysis of two STP effluents discharging into the Weschnitz and the Modau indicate that terbutryn enters the rivers from this source. Furthermore, terbutryn concentrations and loads showed a clear seasonal trend with significantly higher levels in summer and autumn. Obviously, the ban on agricultural use of terbutryn at the end of 2003 had no discernable influence on terbutryn concentrations in the rivers because there was no decreasing trend.

1 Introduction

Over the last decade, the use of chemical compounds in all sectors of human life has significantly increased. Within the European Union, approximately 250 to 300 new chemical substances are registered each year (ECB, 2004). About 10.5 % of these are high production volume chemicals (HPVC) exceeding a production volume of 10 t/a. For many of these chemicals, there is a lack of information regarding their ecotoxicologic behavior and environmental fate. Therefore, this becomes a potential risk to human health and the environment, especially when they enter aquatic ecosystems. These chemicals are typically characterized by high production volumes, high polarity, and low biodegradability. The occurrence of these so-called "emergent pollutants" such as pharmaceuticals, personal care products, surfactants, flame retardants, and industrial and agricultural chemicals in rivers has already been proven by numerous studies (Daughton and Ternes 1999, Kolpin et al. 2002, Boyd et al. 2003, Poiger et al. 2003, Dsikowitzky et al. 2004). Due to their persistence, these substances often pass through sewage treatment plants (STPs) with incomplete degradation or even without any transformation (Fahlenkamp et al., 2004) and can therefore be found in considerable concentrations in receiving waters. Particularly small freshwater streams can receive large amounts of treated wastewater which can make up almost 100 % of the stream water, particularly at low flow conditions. Due to the large private consumption of these substances by the population, the problem also provides a social dimension along with the ecological and economical dimensions. The INTAFERE (Integrated Analysis of Mobile Organic Foreign Substances in Rivers) project was established to investigate the risk potential of organic pollutants for aquatic ecosystems and water resources in an integrative way. The results from hydrochemical, ecotoxicological, and social research are linked within INTAFERE with the objective to draft quantitative and qualitative future scenarios for the occurrence and risk potential of xenobiotics within small river systems. The present study was compiled within the frame of INTAFERE and targets the analysis of xenobiotics in small freshwater streams via hydrochemical monitoring. Therefore, twelve substances fulfilling the attributes of emergent pollutants were chosen with the aim of investigating the temporal and spatial concentration variation within small freshwater streams and to identify possible sources and sinks.

The selected study area was the "Hessisches Ried" region in the south of Frankfurt, Germany, which is one of the major suppliers of drinking water for the city of Frankfurt due to its abundant groundwater reservoirs. Furthermore, the region suffers from strong anthropogenic

impacts by industrial, agricultural, and building activities. The former natural brooks of the region meanwhile have been transformed by human construction activity and continuous input of municipal and industrial wastewater. Therefore, there is a special concern regarding the future development of water quality in this region.

Among the selected substances were the organophosphates tri-n-butyl phosphate (TBP), tris(2-butoxyethyl)phosphate (TBEP), tris(2-chloroethyl)phosphate (TCEP), tris(1-chloro-2-propyl)phosphate (TCPP), and tris(1,3-dichloro-2-propyl)phosphate (TDCPP), which predominantly serve as flame retardants and plasticizers in many consumer products. Due to their favorable characteristics, the organophosphates are often used in products within the plastics, vehicle, building, textile, and furniture industries. In the late 1990s, about 360,000 t/a of flame retardants were applied in Western Europe, thereof 72,000 t/a of organophosphorous flame retardants (Metzger und Möhle, 2001). As organophosphates are mainly used as additives, they can diffuse out of the products and enter the environment via leaching, volatization, or abrasion (Marklund et al. 2003) during the entire lifetime of the product. Congruously, organophosphates have been detected in indoor air (Hartmann et al., 2004), in rain (Fries and Püttmann, 2003a), in influents and effluents of sewage treatment plants (Meyer and Bester, 2004), and in rivers and sediments (Andresen et al., 2004; Dsikowitzky et al., 2004a, Kawagoshi et al., 1999).

In addition, the synthetic musk fragrances 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta-[γ]-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) are chemical products of major economic importance and were subjects of this study. Synthetic musks are predominantly applied as fragrances in personal care products, cleaning products, and detergents. With an annual consumption of 1,427 t/a and 434 t/a respectively, HHCB and AHTN account for 95% of the synthetic musk fragrances consumed in the EU (IFRA, 2002). Synthetic musk fragrances are known to enter the aquatic environment via STP effluents (Eschke, 2004; Simonich et al., 2002) where they have often been detected in rivers (Buerge et al., 2003; Dsikowitzky et al., 2002), lakes (Peck and Hornbuckle, 2004), and sediments (Heim et al., 2004; Kronimus et al., 2004). Due to their ubiquitous occurrence and low biodegradability in sewage treatment plants, HHCB and AHTN have been proposed as markers for domestic wastewaters by some authors (Buerge et al., 2003).

Another group of chemicals of public concern are substances which can affect the endocrine system of aquatic organisms, such as the phenolic xenoestrogens bisphenol A (BPA), 4-tert-octylphenol (4-tert.-OP), and the technical isomer mixture of 4-nonylphenol (NP). Evidence

of estrogenic activity of BPA has been known since the 1930s (Dodds and Lawson, 1936; Dodds and Lawson, 1938). BPA is an important industrial chemical which is used for the manufacture of epoxy, polycarbonate, phenoxy, and polysulfone resins. The production volume of BPA is about 2.8 million t/a on a global scale (Bisphenol A Global Industrial Group, 2004). Although BPA is easily biodegradable (Staples et al., 1998) and therefore largely eliminated in STPs, it has been detected occasionally within effluents (Höhne and Püttmann, 2006a) and receiving waters (Bolz et al., 2001; Scheffknecht, 2005; Stachel et al., 2003). Since the early 1980s, the alkylphenols OP and NP have been frequently detected within STP effluents (Giger et al. 1981) as well as in adjacent receiving waters (Ahel et al., 1994; Schaffner et al., 1987). Alkylphenols are transformation products of alkylphenolethoxylates (APEOs), which are predominantly used as industrial detergents, but also as emulgating agents in pesticides (Guenther et al., 2002) and as aircraft deicers (Corsi et al., 2003). Although there was a voluntary agreement by the producers to abandon the use of APEOs in industrial detergents in 1992 (BMU, 2003), production of nonylphenolethoxylates (NPEOs) and octylphenolethoxylates (OPEOs) in Germany still reached levels of up to 37,000 t/a and 2,000 t/a in 2000 respectively (Leisewitz et al., 2001b).

Besides the organophosphates, the synthetic musk fragrances, and the endocrine disruptors, two more chemicals were included in this study: the herbicide 2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (Terbutryn) as well as the insect repellent N,N-diethyl-m-toluamide (DEET). DEET is often detected in STP effluents and river waters (Dsikowitzky et al., 2004, Knepper et al., 1996) despite voluntary application abandonment by the main producer Bayer in the late 1990s. Until 1999, DEET was the active agent in the insect repellent Autan®, when it was replaced by Bayrepel (1-piperidinecarboxylic acid, 2-(2-hydroxyethyl), 1-methylpropyl ester). Terbutryn is a herbicide of the triazine group and inhibits photosynthesis of pre- and post-emergent weeds. It is preferentially applied in corn, pea, and cereal cultures. Although the license for application as a herbicide in Germany was withdrawn as of 1st January 2004, terbutryn is still used as an aquatic herbicide for control of algae in garden ponds and indoor aquaria, and as a biocide in antifouling paints and coatings.

The target compounds are subject to differing regulations. For example, whereas the use of NP and the related NPEOs were strictly regulated under the EU directive 2003/53/EG in January 2005, the ban of terbutryn as a herbicide in January 2004 was not obligated for all EU members. Other chemicals such as DEET and TCEP were both withdrawn before 2000 under voluntary agreements. Therefore, the impact of the regulation status on the environmental concentrations of these xenobiotics will also be relevant to this study.

2 Study area and experimental design

2.1 Study area

The study area is a region south of Frankfurt am Main, Germany, named "Hessisches Ried", which comprises an area of approximately 1,200 km². Natural boundaries are the Main River in the north, the "Odenwald" mountains in the east, the Neckar River in the south and the Rhine River in the west. From the geological formation, the region forms part of the northern Rhine rift valley and has a predominantly flat landscape. At the beginning of the Tertiary, the Rhine rift valley had sunk and during the following thousands of years it was refilled by accumulations of fluvial, aeolic and cryogenic sediments. These sediments facilitate the storage of large amounts of groundwater and are the reason why today the region is an important resource and supplier of drinking water. Currently, about 800,000 inhabitants in 36 cities and communities live in Hessisches Ried (Rüppel et al., 2002). Besides agricultural and industrial uses, the region is traversed by many means of communication, and therefore suffers from strong anthropogenic impacts.

The drainage area consists of four small river systems: Schwarzbach, Modau, Winkelbach, and Weschnitz (from north to south). These rivers are tributaries to the Rhine River and discharge only small volumes of water, ranging from 0.3 m³/s (Winkelbach) to approx. 3 m³/s (Weschnitz) of water on an annual average (Table 1).

Table 1: Characteristics of investigated fresh water streams

	Schwarzbach	Modau	Winkelbach	Weschnitz
mean discharge [m³/s] a)	2.0	1.1	0.27	3.2
catchment area [km²] a)	478.0	202.0	108.4	414.2
Residence time of water [h]	23	15	12	19
Investigated flow distance [km]	26.8	21.7	15.5	33.6
Mean flow velocity [m/s]	0.32	0.41	0.35	0.49
population equivalent b)	477 600	218 500	95 750	324 050
estimated wastewater proportion at regular flow conditions (mean discharge) % a)	50%	35%	47%	15%

a) Data from Göbel (1996)
b) Data calculated on Data from HLUG (http://www.hlug.de/medien/wasser/abwasser/dokumente/Lagebericht2004_Endfassung_mit_Karten.pdf)

The rivers serve as receiving waters for large amounts of treated wastewater. A total of 28 sewage treatment plants discharge waste water into the rivers, which is accumulated by a population of approx. 1.2 million inhabitants.In warm and dry periods (for example in summer) this can lead to nearly 100 % wastewater content in the rivers (Göbel, 1996). With an annual precipitation of 500 – 600 mm, the region is rather dry (in comparison to the mean annual precipitation in Germany), but receives larger amounts of water from the Odenwald area, where annual precipitation is above 1,000 mm. The rivers' courses emanate from artificial drainage measures in the former Rhine River floodplain about one hundred years ago. The whole area is crisscrossed by more or less actively used draining channels leading to a very complex hydrological discharge system, which is also influenced by further human activities such as flood control and artificial groundwater recharge. The hydrologic situation is therefore rather undetermined. At the lower reaches, all rivers are diked and river beds have been largely converted to artificial trapeze profiles. Figure 1 shows a typical view of a river in the study area.

Figure 1: The Weschnitz River near Lorsch

2.2 Experimental design

Throughout the river systems (Schwarzbach - Landgraben, Modau – Sandbach, Winkelbach and Weschnitz) the sampling sites were chosen in order to map the catchment area in a representative way. Therefore, in each river system a couple of sampling points (5-7) along the rivers' courses were selected, covering first of all the lower reaches of the rivers. The setting of sampling points stopped at the boundary to the Odenwald mountains, where structural patterns of the rivers change due to a strong inclining terrain. Figure 2 gives an overview on the location of sampling points.

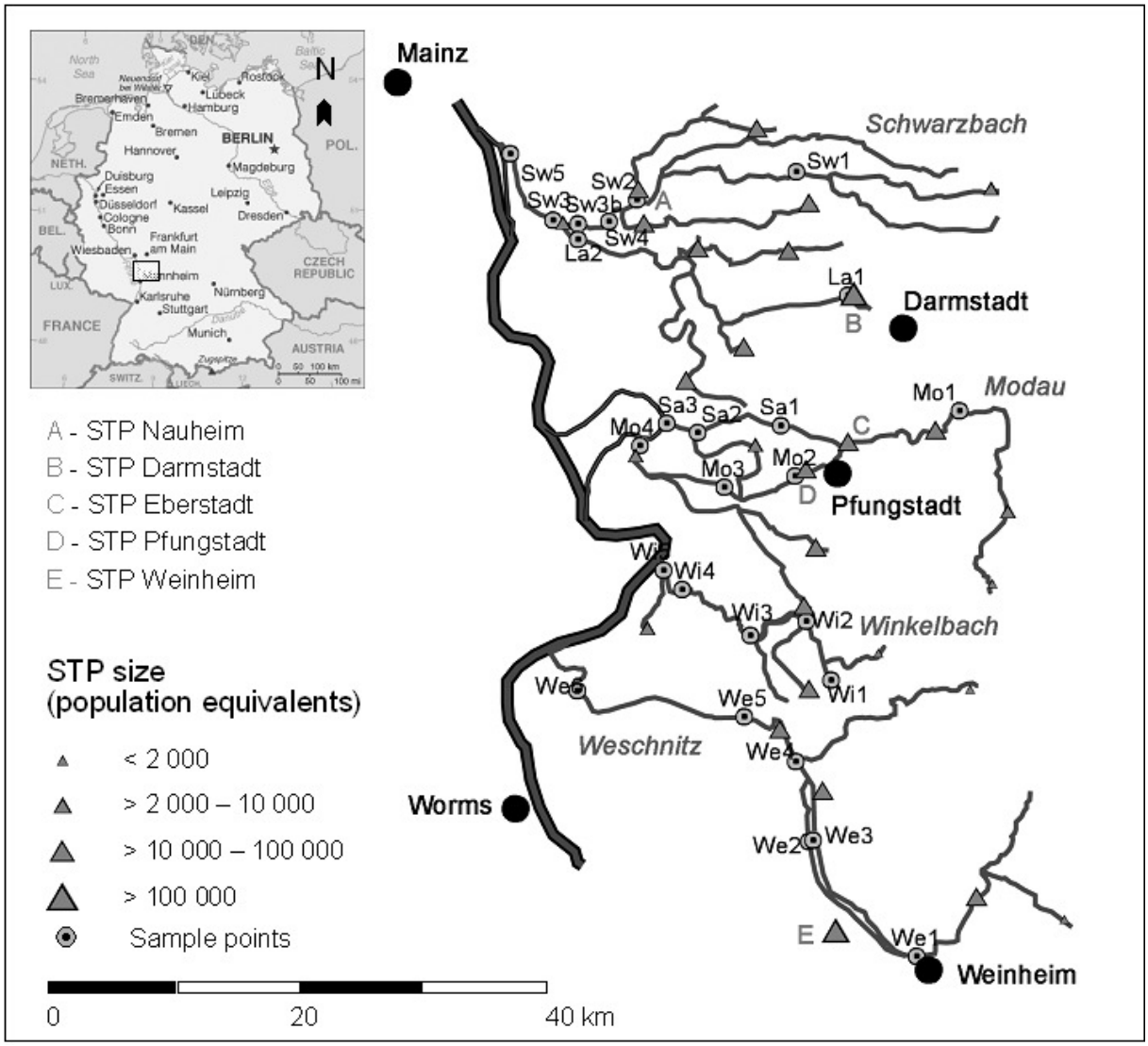


Figure 2: Sampling area and sampling sites

In the northern part of the study area, the Hessisches Ried is drained by the Schwarzbach – Landgraben river system, which was sampled at eight locations, thereof six in the

Schwarzbach River (Sw1−Sw5) and two in the Landgraben River (La1−La2). In the Modau – Sandbach rivers systems the Modau River furcates into the Modau and Sandbach downstream of Pfungstadt, and both join the Rhine River near Stockstadt. Three sampling sites were selected on the Sandbach River (Sa−Sa3) and four were selected on the Modau River (Mo1−Mo4). Along the Winkelbach River, the smallest and shortest of the investigated rivers, five sampling points were determined (Wi1-Wi5). The Weschnitz River in the south of the study area was sampled at six sites (We1−We6). Downstream from Weinheim, the river splits into the so-called 'old' and 'new' Weschnitz River and both rejoin each other near Lorsch. This particularity is reflected by determining a sampling point on the old river (We2) and one on the new (We3). A list of the geographic coordinates (Gauß-Krüger) of the sampling sites is presented in Table 2.

Table 2: Geographic coordinates of sample points

	River	No.	Easting (RW)	Northing (HW)	Distance to the rivers mouth [km]
Modau	Modau	**Mo 1**	34 79 145	55 21 425	21.7
	Modau	**Mo 2**	34 69 935	55 17 770	10.7
	Modau	**Mo 3**	34 65 940	55 17 140	6.9
	Modau	**Mo 4**	34 61 215	55 19 500	1.3
	Sandbach	**Sa 1**	34 69 120	55 20 620	7.2
	Sandbach	**Sa 2**	34 64 890	55 18 930	2.3
	Sandbach	**Sa 3**	34 62 730	55 20 750	0.1
Schwarzbach	Darmbach	**La 1**	34 72 870	55 27 910	26.8
	Landgraben	**La 2**	34 57 725	55 31 040	7.8
	Apfelbach	**Sw 1**	34 69 980	55 34 850	22.7
	Schwarzbach	**Sw 2**	34 61 040	55 33 280	12.8
	Schwarzbach	**Sw 3**	34 56 350	55 32 140	5.9
	Schwarzbach	**Sw 3b**	34 57 670	55 31 110	7.5
	Schwarzbach	**Sw 4**	34 59 460	55 32 055	10.4
	Schwarzbach	**Sw 5**	34 53 655	55 36 140	1.7
Weschnitz	Weschnitz	**We 1**	34 76 740	54 90 815	33.6
	Alte Weschnitz	**We 2**	34 70 685	54 97 280	24.1
	Neue Weschnitz	**We 3**	34 70 945	54 97 340	23.7
	Weschnitz	**We 4**	34 69 960	55 01 760	18.7
	Weschnitz	**We 5**	34 67 055	55 04 275	14.4
	Weschnitz	**We 6**	34 57 690	55 05 735	4.8
Winkelbach	Winkelbach	**Wi 1**	34 71 930	55 06 325	15.5
	Winkelbach	**Wi 2**	34 70 560	55 09 650	12.1
	Winkelbach	**Wi 3**	34 67 410	55 08 835	8.2
	Winkelbach	**Wi 4**	34 63 600	55 11 420	2.5
	Winkelbach	**Wi 5**	34 62 535	55 12 500	0.9

In the time span from September 2003 to September 2006, the rivers were sampled quarterly. During each sampling campaign, a volume of 2.5 l surface water was collected from each of the 26 sampling points. Furthermore, for the later calculation of transported loads, flow velocity and flow profile were measured at each sampling site according to Dyck and Pescke (1995). Therefore, flow profile was divided into several vertical lamellas. Mean flow velocity was determined by one point measurements at 40 % of the water depth. A hydrometric vane from OTT Messtechnik was used for the flow velocity measurements. In addition, some physico-chemical parameters like water temperature, conductivity, and pH-value were recorded at all sampling points.

In June and September 2005, besides the quarterly sampling of surface water, in addition five STP effluents in the catchment area (STP Nauheim, STP Darmstadt, STP Eberstadt, STP Weinheim and STP Pfungstadt) were sampled to estimate the input of target compounds into the rivers. The STP Nauheim and STP Darmstadt discharge into the Schwarbach – Landgraben, STP Eberstadt and STP Pfungstadt into the Modau – Sandbach and STP Weinheim into the New Weschnitz. The location of all STPs within the catchment area as well as their sizes can be obtained from Figure 2.

3 Analytical Methods

3.1 Solid phase extraction (SPE)

Extraction of the target compounds from the water samples was carried out by solid phase extraction (SPE). Therefore SPE cartridges "Bond Elut PPL: 100 mg/ 1ml" from Varian were used. The cartridges are packed with a Styrol-Divinylbenzol-Polymer, which serves as a sorbent and has a low polarity. The solid phase is characterized by a pore size of 150 Å, a particle size of 125 µm and a surface of 700 m²/g. According to the manufacturer's information, this material is suitable for the enrichment of polar and medium polar substances. Before charging the cartridges with a water sample, the sorbent must be preconditioned with a solvent to provoke the lipophile alkyl chains set up and to be suitable for adsorption. Therefore, 1 ml methanol was rinsed over the cartridge (by gravitation). Thereafter, for the cleaning of the cartridge 1 ml methanol/acetonitrile (50:50) was rinsed with a negative pressure of 800 mbar. Cartridges were then filled with 1 ml distilled water. The water samples were connected by PTFE tubes filled with distilled water and passed through the cartridges with a negative pressure of 600 – 800 mbar. The flow rate was kept constant at approx. 300 ml/h. During the whole process it is important to prevent the sorbent from running dry. For the simultaneous extraction of up to 20 samples, the vacuum unit "Vac Elut 20" from Varian was used. Figure 3 shows a picture of the SPE – device.

After extraction, SPE cartridges were dried in nitrogen stream. The cartridges were then eluted into a GC-vial (1.1 ml). Elution was performed in three steps, e.g. the cartridges were eluted three times with 333 µl methanol/acetonitrile mixture (50:50) to enable the extracts to desorb completely from the sorbent. Extracts were then dried in nitrogen stream and resolved in 100 µl acetonitrile. After the addition of the internal standard (4,000 ng squalane) the samples were now ready to proceed to GC-MS-Analysis.

Figure 3: Equipment for solid phase extraction

3.2 GC-MS-Analysis

The GC-MS-Analysis was performed by Fisons gaschromatograph GC 800 (equipped with a BP-X5 capillary column (30 m length, 0.25 mm inner diameter and 0.25 µm film thickness) and the mass detector MD 800 also from Fisons, using electron ionization (EI, 70eV). Helium was used as carrier gas with a pressure of 70 kPa. The sample injection (1 µl) was carried out in splitless mode by the autosampler AS 800. The GC oven temperature program started at 80°C and was raised up to 300°C at the rate of 4°C per minute. After the temperature of 300°C was accomplished it was held constant for a period of 30 minutes. The mass spectrometer was operated in full-scan mode (50 – 600 m/z) under the analysis software "MASSLAB" (Finnigan, 1994). In Table 3 an overview of the applied equipment specifications is given.

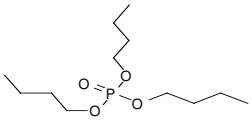
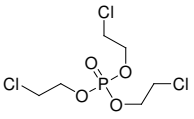
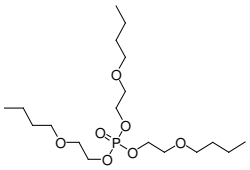
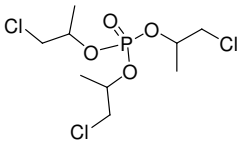
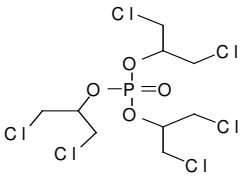
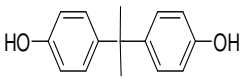
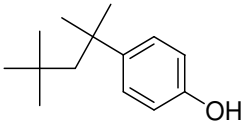
Table 3: Specifications of the equipment

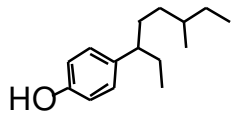
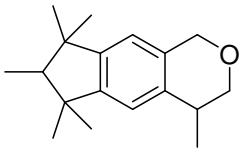
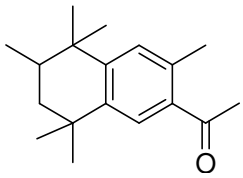
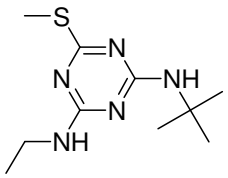
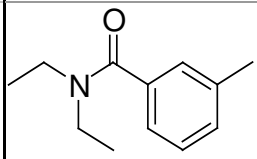
GC: GC 8000 Series	
Capillary column	30 m , 0.25 mm ID, 0.25 µm film thickness
Carrier gas	Helium
Split	splitless
Pressure	70 kPa
Injector temperature	280 °C
Injection volume	1 µg/l
Temperature program	80°C, 4°C per min, 300°C, 30 min
MS: MD 800 (Fisons)	
Scan mode	Full scan
Scan range	50 - 600 m/z
Fragmentation	EI+ /70V
Temperature Ion source	220 °C
Software	Masslab

3.2.1 Target compounds

The target compounds TBP, TBEP, TCEP, TCPP, TDCPP, HHCB, AHTN, BPA, NP, OP, Terbutryn, and DEET were identified comparing the retention times and the mass spectra obtained from pure standard substances. Table 4 summarizes the relevant analysis parameters for the target compounds.

Table 4: Analytic parameters of the target compounds

Name	Structure	Formula	Molecular weight	Qualifier ions	Quantifier ion	Retention time (min)
TBP Tributyl-phosphate		$C_{12}H_{27}O_4P$	266	155, 211	99	25,2
TCEP Tris(2-chlorethyl) phosphate		$C_6H_{12}O_4PCl_3$	285	205, 207, 249, 251	63	29,1
TBEP Tris (2-butoxyethyl) phosphate		$C_{18}H39O_7P$	398	57, 199, 299	125	44,4
TCPP Tris (1-Chloro-2-Propyl) phosphate		$C_9H_{18}Cl_3O_4P$	309	125, 201, 157, 277, 291	99	29,6
TDCPP Tris(1,3dichloro-2-propyl) phosphate		$C_9H_{15}Cl_6O_4P$	431	99, 191, 209, 301, 381	75	42,9
BPA Bisphenol A		$C_{15}H_{16}O_2$	228	213, 228	213	40,5
OP 4-tert.-Octylphenol		$C_{14}H_{22}O$	206	107, 206, 135	135	24,2

NP 4-Nonylphenol (isomer mixture)		$C_{15}H_{24}O$	220	see 5.3.3.	135, 121, 177, 149	24.5-27.3
HHCB 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-g-2-benzopyran		$C_{18}H_{26}O$	258	213, 258	243	30.9
AHTN 7-Acetyl-1,1,3,4,4,6 hexamethyl-tetralin		$C_{18}H_{26}O$	258	258	243	31.1
Terbutryn N-(1,1-dimethylethyl)-N'-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine		$C_{10}H_{19}N_5S$	241	185, 170, 241	226	33.8
DEET N,N-diethyl-m-toluamide		$C_{12}H_{17}NO$	191	91, 190	119	23.5

3.2.2 Quantification

The quantification of target compounds was based on the internal standard calibration method. Therefore, the peak area of the internal standard (IS) squalan in the Total Ion Chromatogram (TIC) of each sample had to be compared to the peak areas of the target compounds in the mass trace (m/z). The calculation of the target compound concentration in the water sample was performed according to the following equation.

$$\mathbf{C(compound)_{water}\ [ng/l] = A\ (compound)_{m/z}/A\ (IS)_{TIC} * m(IS) * K/R * 1/V}$$

$C(compound)_{water}$	Concentration of target compound in the water sample
$A\ (compound)_{m/z}$	Peak Area of target compound in the mass trace
$A\ (IS)_{TIC}$	Peak Area of the IS in the TIC
m(IS)	Mass of applied IS (i.e. 4,000 ng)
K	Correction factor
R	Response factor
V	Volume of the water sample (i.e. 2.5 l)

While the correction factor K represents the relation of the peak area of a compound in the TIC compared to their peak area in the mass trace, the response factor R reflects the ratio between the peak areas of a compound and the IS within the TIC.

$$\mathbf{K = A\ (compound)_{TIC}/A\ (compound)_{m/z}}$$

$$\mathbf{R = A(compound)_{TIC}/A\ (IS)_{TIC} * m(IS)/m(compound)}$$

$A\ (compound)_{TIC}$	Peak Area of target compound in the TIC
$A\ (compound)_{m/z}$	Peak Area of target compound in the mass trace
$A\ (IS)_{TIC}$	Peak Area of the IS in the TIC
m(IS)	Mass of applied IS
m(compound)	Mass of applied target compound

Both factors had to be calculated for each series of measurements on the basis of measurements of the pure standards of the target compounds. Table 5 shows the values for the correction factor K and the response factor R in September 2006.

Table 5: Values for the correction factor K and the response factor R during the measurements in September 2006

	m/z	K	R
DEET	119	2.77	0.70
Octylphenol	135	3.13	0.83
TBP	99	3.36	0.71
TCEP	63	4.84	0.44
TCPP			
Isomer 1	99	6.0	0.81
Isomer 2	99	5.03	0.57
BPA	213	2.81	0.2
TDCPP	75	5.42	0.6
TBEP	125	17.53	0.7
Nonylphenol			
Isomer 1	149	5.1	0.46
Isomer 2	135	2.5	0.46
Isomer 3	121	3.9	0.46
Isomer 4	107	21.0	0.46
HHCB	243	5.39	1.13
AHTN	243	5.45	0.70
Terbutryn	226	10.24	1.15

3.2.3 Validation of the analysis method

For each target compound the limit of detection (LOD), the limit of quantification (LOQ), as well as the recovery rate (RC) had to be determined. Therefore, a series of measurements of pure standard substances at different concentration levels of 0.5 ng/l, 1 ng/l, 2 ng/l, 5 ng/l, 20 ng/l, 50 ng/l, 100 ng/l, 200 ng/l, 1,000 ng/l, and 2,000 ng/l for each target compound were carried out. The measurements at each concentration level were repeated five times and analyzed with respect to the obtained peak areas of the chromatograms. According to the German DIN standard 32645, the LOD can be calculated as follows:

$$\mathbf{LOD = \Phi_{n;\,\alpha} * s_L / b}$$

$\Phi_{n;\,\alpha}$	Factor for quick estimation of x_{LOD}, depending on the desired significance level α and the number n of measurements
s_L	Standard deviation of the measured values of the blank
b	Slope of the calibration line

Considering a significance level of 0.05 and 5 measurements per concentration level the factor $\Phi_{5;0.05}$ accounts for 2.3. For instance, in case of Terbutryn, the standard deviation of the intercept of the calibration line (which is identical with the standard deviation of the blank value) is 22517 and the slope of the calibration line 11960. Therefore, the LOD for Terbutryn of this method is 4.3 ng/l. In figure 4, the calibration line is shown for Terbutryn.

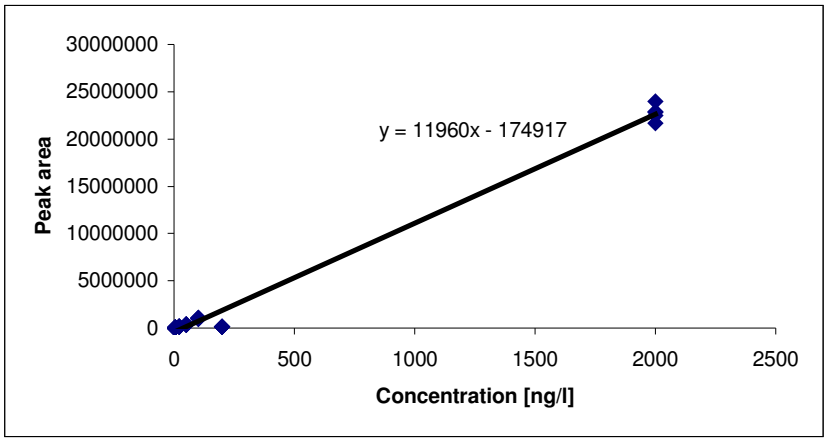


Figure 4: Calibration line for Terbutryn

The LODs of the target compounds ranged between 4 ng/l (TCPP) and 18 ng/l (BPA). According to DIN 32645, the limit of quantification can be estimated as follows:

$$\mathbf{LOQ\ [ng/l] = 3 * LOD\ [ng/l]}$$

The recovery rates were calculated according to the following equation:

$$\mathbf{RC\ [\%] = C_{measured}/C_{expected} *100\%}$$

The mean recovery rates for the target compounds were between 74 % (TBEP) and 104 % (AHTN) and are presented in Table 6.

Table 6: Quantification parameters of the target compounds

	LOD [ng/l]	LOQ [ng/l]	RC [%]
OP	9.8	29.3	84
NP	8.4	25.3	77
HHCB	5.8	17.4	94
AHTN	6.2	18.7	104
TDCPP	3.8	11.4	82
TCPP	3.6	10.9	78
TnBP	5.6	16.8	101
DEET	7.8	23.3	81
Terbutryn	4.3	13.0	80
BPA	18.4	55.3	86
TCEP	4.8	14.3	110
TBEP	3.6	10.7	74

4 Organophosphates and synthetic musk fragrances in freshwater streams in Hesse, Germany

4.1 Abstract

Four small freshwater river systems in Hesse, Germany, have been investigated with respect to seasonal and spatial concentration variations and transported load of the organophosphates tri-n-butyl phosphate (TBP), tris(2-butoxyethyl)phosphate (TBEP), tris(2-chloroethyl)phosphate (TCEP), tris(1-chloro-2-propyl)phosphate (TCPP), and tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and the synthetic musk fragrances 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta-[γ]-2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN). Data originate from water samples collected in the time span from September 2003 to April 2005 at 25 sampling locations. The detection frequency for all compounds was about 90%. Mean concentration levels of organophosphates were 502 ng/l (TCPP), 276 ng/l (TBP), 183 ng/l (TBEP), 118 ng/l (TCEP) and 117 ng/l (TDCPP). The synthetic musk fragrances HHCB and ATHN were detected with mean concentrations of 141 ng/l and 46 ng/l, respectively. The variability of the concentration of all compounds was high with respect to space and time. The highest concentrations were observed in the Schwarzbach system characterized by the highest proportion of waste water compared to the other river systems. Concentration levels of synthetic musk fragrances were significantly lower in summer times compared to winter times.

STP effluents were identified as the dominating source for the analyzed substances in the river systems. Also diffuse sources can cause locally high concentrations of the compounds in stream areas not influenced by STPs. On average, the amount of transported load increased from the source to the mouth of the rivers, indicating that input amount exceeds the elimination capacity within these small river systems. However, the overall load of the compounds in the river systems was generally lower compared to other systems studied previously.

4.2 Introduction

During the last decades, usage of chemical compounds in all sectors of human life has been of growing importance. The total number of used chemical substances increased significantly.

According to the European Chemical Bureau (http://ecb.jrc.it/new-chemicals/) within the European Union, 250 to 300 new chemical substances are registered every year, 10.5 % of which are manufactured at production levels above 10 t/a. Today, there is a large variety of chemical compounds that can enter the environment due to human activities. Several of these contemporaneous organic pollutants such as personal care products, pharmaceuticals, antioxidants, plasticizers and flame retardants are known to pass sewage treatment plants (STPs) with incomplete degradation or even without any transformation (Fahlenkamp et al., 2004) and therefore can be found in considerable concentrations in the receiving waters (Boyd et al., 2003; Kolpin et al., 2002).

Both, synthetic musk fragrances and organophosphates are chemical products of major economic importance and higher production levels. According to Metzger and Möhle (2001), consumption of organophosphate flame retardants in 1998 in Western Europe added up to 72,000 tons. An increase in consumption was predicted at that time. For synthetic musk fragrances annual consumption levels in the EU were reported to have been decreasing since the early 1990s (http://www.ospar.org). However, there are still considerable volumes circulating: in 2000 about 1,427 t/a of HHCB and 434 t/a of AHTN (both substances account for 95 % of synthetic musk fragrances) were consumed in the EU (IFRA, 2002, cited in http://www.ospar.org). Because of high consumption levels and partial persistence against biodegradation congruously, both substance groups show a ubiquitous occurrence and can be found in various environmental compartments: organophosphates have been detected in rivers (Andresen et al., 2004; Dsikowitzky et al., 2004a), sediments (Kawagoshi et al., 1999), rain (Fries and Püttmann, 2003a), raw water (Stackelberg et al., 2004), indoor air (Hartmann et al., 2004), and in pine needles (Aston et al., 1996).

Similar ubiquitous distributions in the environment are observed for synthetic musk fragrances: AHTN and HHCB were detected in rivers (Buerge et al., 2003; Dsikowitzky et al., 2002), lakes (Peck and Hornbuckle, 2004), sediments (Heim et al., 2004; Kronimus et al., 2004), estuaries (Oros et al., 2003), air (Kallenborn et al., 1999; Peck and Hornbuckle, 2004), and rain (www.greenpeace.org/multimedia/download/1/258905/0/rainwater.pdf). A detailed overview of synthetic musk fragrances in the environmental compartments has been presented by Rimkus (2004).

Both, synthetic musk fragrances and organophosphates are known as common ingredients of wastewater and effluents of STPs (Eschke, 2004; Meyer and Bester, 2004; Simonich et al., 2002). The compounds have been proposed by some authors (Buerge et al., 2003;

Dsikowitzky et al., 2004a) to be appropriate markers for the contribution of domestic wastewater to rivers and lakes. Although today measured concentration levels of both compound groups occur usually in the range of trace concentration (nanogram or lower microgram per liter range), an adverse effect on aquatic organisms or even an impact on human health cannot be strictly excluded. Particularly small freshwater streams sometimes receive large amounts of treated wastewater which can make up almost 100 % of the stream water particularly at low flow conditions. So far, only a few studies focused on synthetic musk fragrances and organophosphates in small river systems and provided a quantitative report of transported downstream load in rivers. Kolpin et al. (2004), for example, investigated the behaviour of organic wastewater contaminants during different flow conditions of streams and pointed out that urban contributions of organic contaminants to wastewater become muted as stream flow increases. However, in this study the sampling subject was a large river system in Iowa which discharges at low flow conditions amounts of wastewater exceeding more than 10 times the amounts we deal with in our case. Dsikowitzky et al. (2004b) measured transported loads of various organic contaminants along a longitudinal section of the Lippe River in Germany and classified three distribution types depending on input situation and physico-chemical properties of the compounds. Three of the compounds (notably TCEP, AHTN, and HHCB) which they classified as potential anthropogenic markers are also subject of the present study. Nevertheless, due to larger discharge amounts the Lippe River will show hydraulic characteristics different from those known of small streams or even brooks. Therefore, the aim of the present study is to investigate the fate and behaviour of organophosphates and synthetic musk fragrances in small freshwater streams with special focus on transported load.

4.3 Sampling area and analytical methods

4.3.1 Sampling area

For this approach, a region in the south of Frankfurt, Germany, named “Hessisches Ried” was chosen. The Hessisches Ried is a densely populated and industrialized area whose former natural draining streams/brooks have meanwhile suffered strong anthropogenic impact and transformation by human construction activity and continuous input of municipal and industrial wastewater. Concurrently, the region is one of the major suppliers of drinking water for the city of Frankfurt due to its abundant groundwater reservoirs and therefore relies on particular attention concerning future development of water quality.

The region is drained by four river systems as listed below (from north to south): Schwarzbach, Modau, Winkelbach, and Weschnitz (Figure 2). All of them flow from east to west and are tributaries to the Rhine River. Nevertheless, the river systems show different characteristics concerning discharge volumes: The Weschnitz River is the biggest one of them discharging about 3 m³/s of water on annual average. Schwarzbach and Modau are slightly smaller rivers with a discharge of only 2 and 1 m³/s, and finally Winkelbach drains a water volume of only 0.3 m³/s on annual average. The rivers receive abundant treated wastewater (Table 1) ranging from 15 % in Weschnitz to 50 % in Schwarzbach. For all of the river systems the former natural profiles of the river beds were largely converted to artificial trapeze profile.

Water sampling took place over a period from September 2003 to April 2005 with 7 sampling campaigns at intervals of 2 to 4 month, leading to an overall sample amount of 175 samples. During each sampling campaign a volume of 2.5 l of surface water was collected on each of the 25 sampling points. Water samples were obtained from the middle of the stream, filled into 2.5 l brown glass bottles and stored under cool conditions at 4°C till processing in the laboratory For description of rivers' actual physico-chemical state, some parameters like water temperature, conductivity, and pH-value were recorded at all sampling points. Furthermore, the actual discharge volume was determined measuring the flow profile and velocity. Flow velocity was determined using a hydrometric vane from OTT Messtechnik.

4.3.2 Sample preparation and analysis

Water samples were filtered through paper filters (597½ , Schleicher & Schuell) to remove coarse particles and suspended solids. For extraction of target polar compounds, the analytical method described by Fries and Püttmann (2001) was adopted. This method is based on Solid Phase Extraction (SPE) of the water samples by use of Bond Elute PPL (Varian, 100 mg/1 ml) cartridges. After extraction 4,000 ng of squalane was added as internal standard to each extract.

The samples were analyzed by coupled gas chromatography-mass spectrometry. The gas chromatograph was a Fisons GC 800, equipped with a BP-X5 capillary column (30 m length, 0.25 mm inner diameter and 0.25 µm film thickness). Sample volume of 1 µl extract was injected in splitless mode. GC oven temperature program started at 80°C and was raised up to 300°C at the rate of 4°C per minute. Helium was used as carrier gas. Mass spectrometry was performed with a Fisons MD 800 using electron ionization (EI, 70eV) and operating in Full Scan mode.

The target compounds HHCB and AHTN for synthetic musk fragrances as well as TBP, TBEP, TCEP, TCPP, and TDCPP for organophosphates were identified by mass spectra and retention time (Table 7). For quantification of target compounds the internal standard method with squalane was applied.

For this method, limits of detection (LOD) varied between 3 ng/l for TCPP and AHTN, 5 ng/l for HHCB and TCEP, 6 ng/l for TBEP, 7 ng/l for TBP and 20 ng/l for TDCPP.

Chemical standard substances were purchased from Ehrenstorfer (HHCB and AHTN), Akzo Nobel (TCPP and TDCPP) and Sigma Aldrich (TBP, TBEP and TCEP).

Table 7: Analytical and physicochemical parameters of target compounds

		Identifier Ion	Retention time	Boiling point	Vapor pressure	Henry´s law constant
	CAS-Nr.	m/z	min	°C	Pa	Pa*m³/mol
HHCB	1222-05-5	243	31.2	330 [a)]	0.073 [b)]	11.3 [b)]
AHTN	1506-02-1	243	31.4	180 [c)]	0.068 [b)]	12.5 [b)]
TBP	126-73-8	99	25.4	289 [d)]	0.014 (20°C) [d)]	0.015 [e)]
TBEP	78-51-3	75	44.6	330 [c)]	6.4 (20°C) [c)]	0.003 (20°C) [c)]
TCEP	115-96-8	63	29.3	215 ... 228 [f)]	0.0025 [c)]	0.0000012 [c)]
TCPP	13674-84-5	99	29.9	235 -248 [f)]	100 (20°C) [c)]	0.00604 (25°C) [c)]
TDCPP	13674-87-8	125	43.1	236 [e)]	12 [e)]	0.01 (30°C) [e)]

a) HERA (http://www.heraproject.com/files/04-pcm%20HHCB%20HERA%20Human%20Health%20DISCL%20ed2.pdf), b) Peck & Hornbuckle (Peck and Hornbuckle, 2004), c) ESIS/UICLID (http://ecb.jrc.it/ESIS/), d) Riddick et al. [(Riddick et al., 1985)], e) SRC (http://esc.syrres.com/interkow/physdemo.htm) and f) Enius AG (http://enius.de/schadstoffe/tcep.html)

4.4 Results and discussion

4.4.1 Synthetic musk fragrances

Synthetic musk fragrances were detected in most of the 175 samples collected from September 2003 till April 2005. The concentrations ranged from <5 to 678 ng/l for HHCB and from <3 to 299 ng/l for AHTN, respectively. Table 8 gives an overview of determined statistic variables of measured concentrations. These values are within the scope of prior investigations in the year 2000 that found HHCB and AHTN at mean concentration of 115 ng/l and 46 ng/l in Hessian rivers (Fooken, 1997).

Table 8: Measured concentrations of target compounds [ng/l]

		Organophosphates					Synthetic musk fragrances	
		TBP	**TBEP**	**TCEP**	**TCPP**	**TDCPP**	**HHCB**	**AHTN**
N	**Valid**	175	175	175	175	175	175	175
	< LOD	6	12	22	2	21	11	18
Minimum		< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Maximum		3889	1773	557	2914	1284	678	299
Std. Deviation		365	259	108	413	165	122	43
Mean		**276**	**183**	**118**	**502**	**117**	**141**	**46**
Median		187	86	97	417	80	123	39

According to our measurements, the HHCB/AHTN concentration ratio is almost constant with a value of 3 (correlation coefficient between HHCB and AHTN $R = 0.95$). This observation corresponds with results of Buerge et al. (2003), reporting a mean concentration ratio of 2.6 for HHCB/AHTN. The HHCB/AHTN concentration ratio found in the streams coincides also with the relation of consumption level of HHCB in comparison to that of AHTN (comparing production data cited above).

A seasonal variation with significant lower concentration levels in summer compared to winter and spring/autumn could be observed for both substances (Figure 5). As the calculated loads follow the same trend this effect cannot be explained by discharge variation only. Summer time usually comes along with raised water temperatures and higher intensity of solar radiation. Both aspects could have led to lower concentration levels for polycyclic musk fragrances: increasing ambient temperatures reinforce evaporation of the compounds from the water body, and increasing intensities of solar radiation can be expected to enhance photodegradation of synthetic musk fragrances (Buerge et al., 2003).

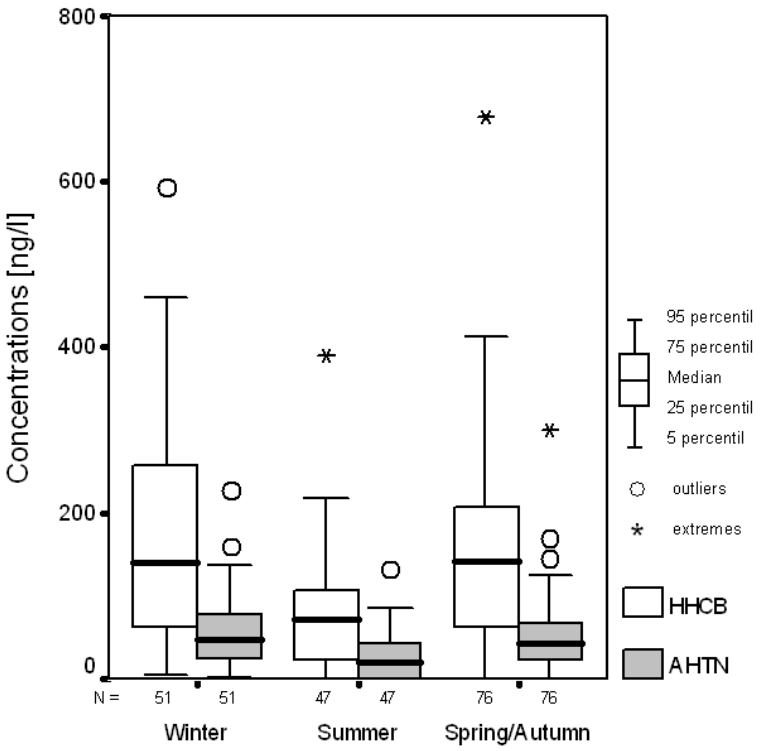


Figure 5: Seasonal variation of HHCB and AHTN concentrations

According to simultaneously performed temperature measurements within the streams average water temperatures in these largely unshadowed shallow streams amount to over 20°C in summer time, to around 12°C in spring and autumn and only 4°C in the winter period. Such seasonal differences in temperature levels of the surface waters are important since volatilization has been proven to be one of the major loss mechanisms of synthetic musk fragrances in Lake Michigan (Peck and Hornbuckle, 2004). In the same study Henry's law constants of HHCB and AHTN has been reported to be in the same range accounting for 11.3 Pa*m³/mol and 12.5 Pa*m³/mol, respectively. Therefore, no major difference in volatilization behaviour of both substances is expected and supposed volatilization loss will not change the concentration ratio of HHCB and AHTN in the surface waters.

Highest concentrations of both synthetic musk fragrances were generally measured in the Schwarzbach River and lowest concentrations in Winkelbach, averaging at 212 ng/l and 61 ng/l for HHCB and at 73 ng/l and 23 ng/l for AHTN, respectively. Concentration levels of Modau and Weschnitz were in between these values, accounting for mean HHCB concentrations of 145 ng/l and 115 ng/l and for mean AHTN concentrations of 44 ng/l and

34 ng/l, respectively. A comparable ranking results when the value for the population equivalent of associated STP effluents is considered: the Schwarzbach River receives the highest amount of treated wastewater which equates to a population equivalent of around 480,000, whereas in Winkelbach the population equivalent accounts only for 95,000 (Table 1). In the Schwarzbach system STPs are situated all along the rivers course, influencing all Schwarzbach sampling points. In contrast, Winkelbach obtaines higher amounts of treated wastewater only nearby the rivers mouth (Wi4 and Wi5). Therefore, the measured concentrations of synthetic musk fragrances reflect very well the impact of wastewater input into the streams.

In addition, higher concentration levels were detected in samples collected nearby STP effluents compared to sampling points more distant from STP effluents (Figure 6). At sampling points in a range of up to 1 km downstream from a STP effluent, the concentrations of the analytes tend to be increased due to the wastewater influence. The ability of synthetic musk fragrances to serve as markers for domestic wastewater has been discussed in various reports before (Buerge et al., 2003; Dsikowitzky et al., 2002; Eschke, 2004) and is appropriate for qualitative implication. However, it is still difficult to establish a quantitative relation between measured concentrations of synthetic musk fragrances and the amount of wastewater input.

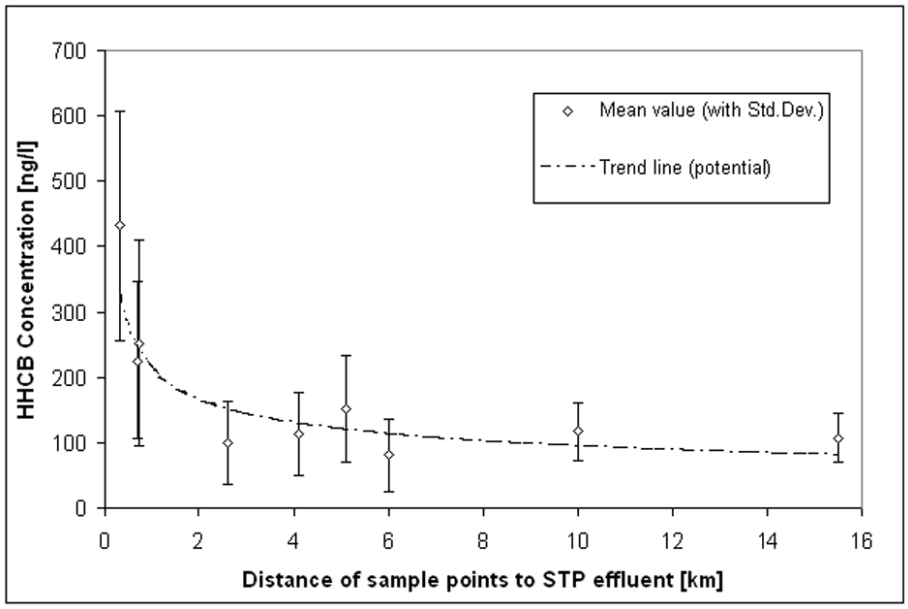


Figure 6: Releation between HHCB concentration and effluent distance

4.4.2 Organophosphates

Concentrations of organophosphates measured in 175 water samples are presented in Table 8. Similar to synthetic musk fragrances the organophosphates TBP, TBEP, TCEP, TCPP, and TDCPP were common constituents of the analyzed water samples with detected frequencies of 97 %, 93 %, 87 %, 99 % and 88 %, respectively. Concentration levels ranged from <7 ng/l up to 3.9 µg/l (in case of TBP) with a strong temporal and spatial variation. TCPP is present in the highest overall concentrations with a mean concentration of 502 ng/l, whereas mean concentrations of TBP, TBEP, TCEP, and TDCPP are noticeably lower (276 ng/l, 183 ng/l, 118 ng/l and 117 ng/l, respectively). Only in a few samples (10) the concentration of TBP exceeded the TCPP concentration by a factor of more than 3. TBP concentrations were already measured in Hessian rivers in the years 1999 – 2001. The reported values were slightly higher than in other parts of Germany (Leisewitz et al., 2001b). This trend seems to continue and suggests a specific impact situation for TBP at a special restricted area, whose origin remains unexplained as long as no more detailed data on effluent disposal are available. However, median concentrations of detected organophosphates lie within the range previously reported for German rivers in other studies (Andresen et al., 2004; ARGE-ELBE, 2000; Dsikowitzky et al., 2004b; Fooken, 1997), and were highest in Schwarzbach and lowest in Winkelbach. This again reflects the amount of wastewater input into both rivers and suggests that STPs are the dominating source for the organophosphates in the streams. Furthermore, sampling points near STP effluents tend to show higher concentration levels for TCPP and TCEP as well. In contrast, variations within the concentrations of the nonchlorinated organophosphates were so large that no spatial patterns could be observed. Detected maximum values correspond largely with concentration levels that can be found in Hessian STP effluents (Höhne and Püttmann, 2006b). The highest concentrations (values that differ more than standard deviation from the mean value) of organophosphates show a higher frequency in the Schwarzbach River, at sampling points near STP effluents and close to the river's mouth. In some cases such as the TDCPP maximum in April 2005, the source can be easily identified by looking at the spatial distribution of concentrations within the river's course (Figure 7).

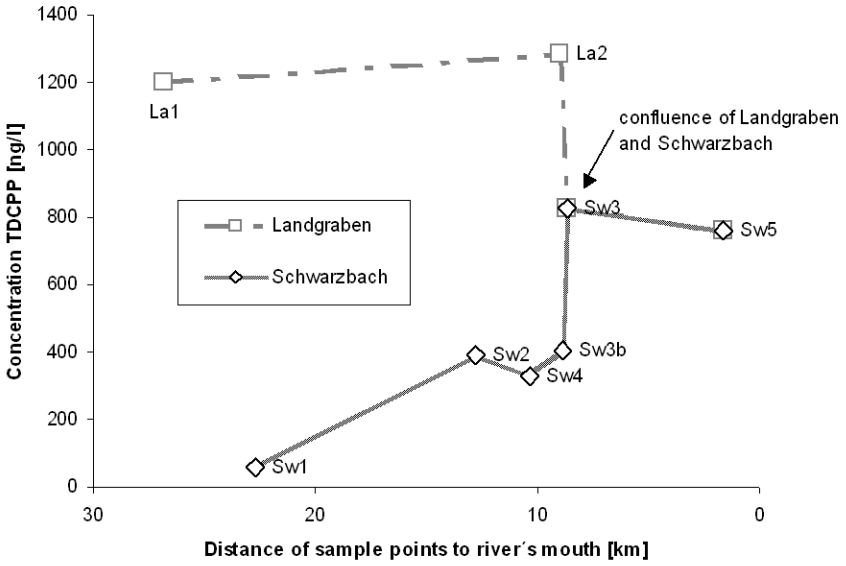


Figure 7: TDCPP concentrations [ng/l] in April 2004 along the Schwarzbach River

The high concentrations of TDCPP obviously originate from an STP effluent that is located only 600 m upstream of La1. Downstream from this sampling point, the concentration remains largely around the high level of 1,200 ng/l till the confluence of Landgraben and Schwarzbach at Sw3. Here, the concentration decreases to 825 ng/l and remains almost at this level till to the mouth of the river (Sw5). Nevertheless, there are some findings that cannot be explained by particular spatial or temporal patterns. For example, the overall TCPP maximum was found in Winkelbach Wi5 in June 2004, accounting for 2,914 ng/l whereas during other sampling periods at the same place the TCPP concentrations were noticeably lower (about 10 to 3 times). This maximum seems to occur as single event and the particular source remains unknown. Possibly, diffuse sources like field run-off or temporarily limited inputs into the sewage system might cause such an extraordinary event. Furthermore, fluctuating STPs purification efficiency and thus varying effluent concentrations have to be considered as a possible reason for the observation.

The concentrations of the chlorinated organophosphates correlate with each other: i.e., when concentrations of TCPP in a sample were high, then concentrations of TCEP and TDCPP were elevated too. Based on correlation coefficients (according to Pearson, significant at the 0.01 level, 2-tailed), a medium correlation between TCPP and TCEP ($R = 0.7$) as well as between TCPP and TDCPP ($R = 0.5$) and a rather feeble correlation between TCEP and TDCPP ($R = 0.3$) is visible. A possible reason for the observation could be that these three chlorinated organophosphates serve in the same field of application as flame retardants e.g. in

polyurethane foam. In contrast, such an effect could not be observed with respect to the nonchlorinated organophosphates. There is no significant correlation between TBP and TBEP and also no correlation between one of them and a chlorinated organophosphate. In addition, a good correlation between TCPP and synthetic musk fragrances was detected (TCPP*HHCB $R = 0.7$, TCPP*AHTN $R = 0.6$). This is not surprising considering that chlorinated organophosphates are nearly persistent to degradation in STPs (Höhne and Püttmann, 2006b; Meyer and Bester, 2004), and likewise synthetic musk fragrances are common ingredients of STP effluents. Prösch et al. (2000) proposed to use TCPP as an appropriate marker for domestic wastewater due to its ubiquitous occurrence and persistence to biodegradation. This is supported by the results from the present study indicating that the overall concentrations of TCPP correlate with the concentrations of synthetic musk fragrances.

No temporal trends in the variation of organophosphate concentrations have been detected which differs from the observations described for synthetic musk fragrances. Possible reasons could be that organophosphates are not susceptible to photodegradation and furthermore own a Henry coefficient that is about three orders of magnitude lower compared to synthetic musk fragrances (Table 7). Therefore, organophosphates will evaporate at significant lower levels compared to synthetic musk fragrances, and loss of organophosphates by evaporation from the water body will be negligible both in summer and winter seasons.

4.4.3 Discharge and estimated loads

Flow conditions of the four investigated streams reached neither lowest nor highest discharge levels relative to reported statistics of long-time measurements in any sampling period. Thus, the differences in discharged water volumes were greater within the sampled river itself (from one sample point to another) than from one sample period to the following.

Nevertheless, a temporal variation in discharge could be noticed: For all observed river systems discharge was lowest in June 2004 and highest in April 2005, except for the Schwarzbach River, whose discharge maximum was in December 2004. Figure 8 shows the different flow conditions during sampling periods exemplified by the measured discharge volumes at representative sampling points. Differences in temporal distribution of discharge maxima depend on the catchment area: Modau, Winkelbach, and Weschnitz originate from a mountainous region called “Odenwald” and receive more natural run-off and are therefore subjected to seasonal rain variations, whereas Schwarzbach is supplied by only a few small lowland brooks and subjected to a larger degree to STP input.

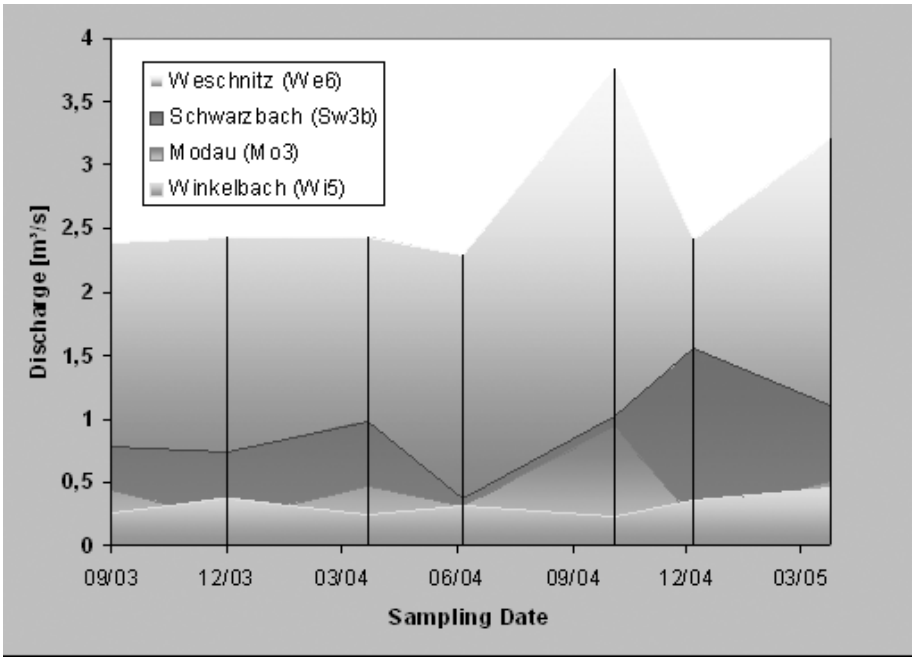


Figure 8: Flow conditions at different sample points during sampling period from September 2003 to April 2005

Consequently, one could presume that at higher discharge levels dilution leads to lower concentration levels of transported organic contaminants. However, this seems only true for larger rivers, where discharge variance exceeds the amount of introduced wastewater by a multiple. In our case, no correlation between the amount of discharged water and measured concentrations could be observed: more precisely, discharge variation had no significant effects on measured concentration levels, neither for synthetic musk fragrances nor for organophosphates. Furthermore, dilution effects at higher discharge levels cannot be observed. As mentioned above, temporal discharge differences at sample points were marginal: two thirds of measured discharge volumes differ only by about 0.2 m³/s from the corresponding mean value. This difference is very low considering that a major STP like the plant of Weinheim (situated in the sampling area and treating a population equivalent of 180,000) on average discharges about 0.4 m³/s. In addition, STPs are sometimes forced to pass untreated wastewater mixed with rainwater into the receiving streams due to a high hydraulic load during heavy rainfall events. In this case, discharged rainwater can contain higher loads of organic pollutants. Furthermore, heavy rainfall events can also affect elimination efficiency of STPs, as Ternes (2000) demonstrated for polar drugs.

The Weschnitz River is characterized by a higher amount of transported load because of higher discharge volumes compared to the other river systems: average loads at the river's mouth accounted for 29 g/d HHCB, 7 g/d AHTN, 97 g/d TCPP, 16 g/d TCEP, 43 g/d TDCPP,

41 g/d TBP, and 22 g/d TBEP. Mean loads from the other river systems are lower and are shown in

Table 9. These values are generally lower than the values presented by Dsikowitzky et al. (2004b) for the Lippe system and by Bester (2005) for the Ruhr system. This can be explained by the higher discharge amounts of Lippe and Ruhr rivers, respectively.

Table 9: Calculated mean loads of target compounds [kg/a]

	Weschnitz	Schwarzbach	Winkelbach	Modau
TCPP	34.4	15.9	7.2	13.9
TCEP	5.9	4.1	1.0	2.3
TDCPP	15.5	1.9	1.1	2.7
TBP	15.1	6.2	1.8	4.4
TBEP	8.1	2.6	1.2	2.2
HHCB	10.1	5.0	1.2	3.4
AHTN	2.7	1.7	0.4	1.0

Some findings are remarkable considering transported load along river's length. There was an increase in transported load of all investigated substances with increasing river's length. HHCB and TCPP loads are exemplarily presented in Figure 9 (note: only data from consecutive sample points are presented). In all river systems, load increased and reached its maximum at river's mouth except for Schwarzbach river whose ultimate sample point lies within the range of the Rhine river's tailback and therefore may have had a dilution effect on measured concentrations and determined loads as well. However, the increment of transported load from the source to the mouth of the rivers, indicates that input amount exceeds the elimination capacity within these small river systems. Except for the nonchlorinated organophosphates TBP and TBEP, target compounds are regarded to be poor or not biodegradable. Biodegradation of TBP and TBEP was observed to take several days in surface waters (Ernst, 1988; Saeger, 1979). With respect to the investigated rivers, at mean flow velocity of 0.4 m/s and maximal flow distances of about 30 km to the river's mouth (Table 1) detention time of target compounds is only about 20 hours. Therefore biodegradation can be expected to be limited and target substances will preferentially be exported to the Rhine River, if not bound to the sediment or degraded photochemically.

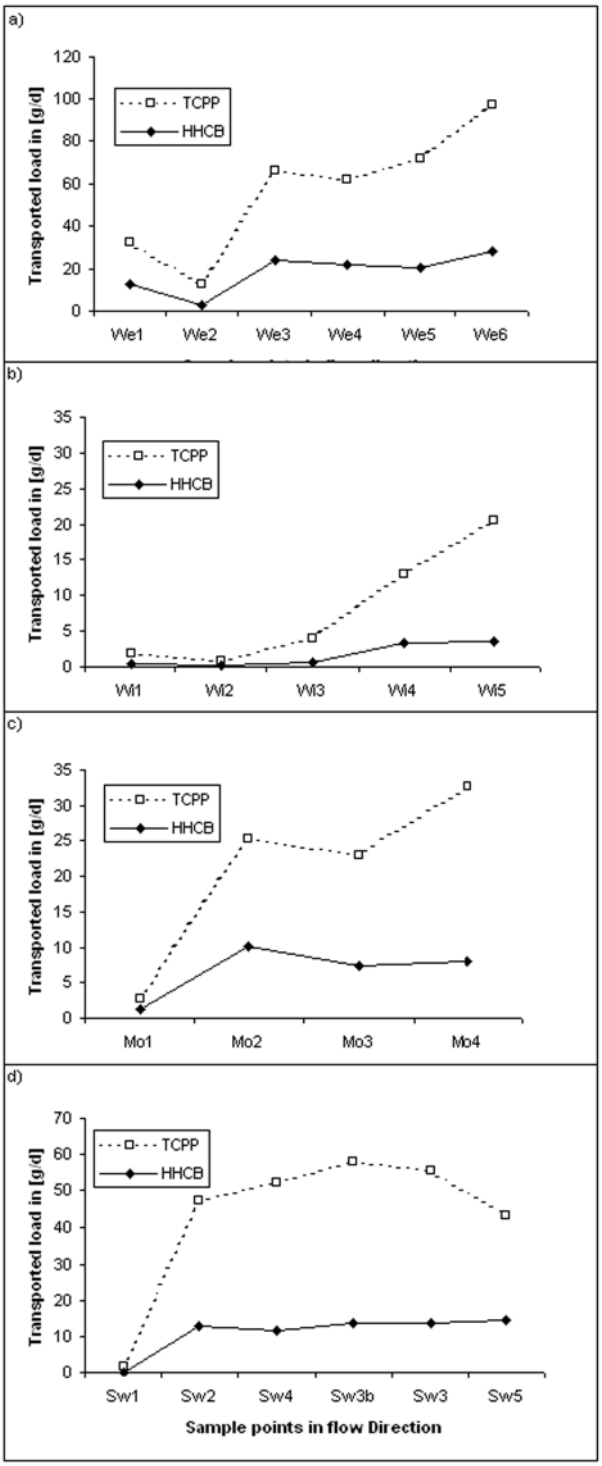


Figure 9: Mean HHCB and TCPP load [g/d] in Weschnitz (a), Winkelbach (b), Modau (c) and Schwarzbach (d) in flow direction

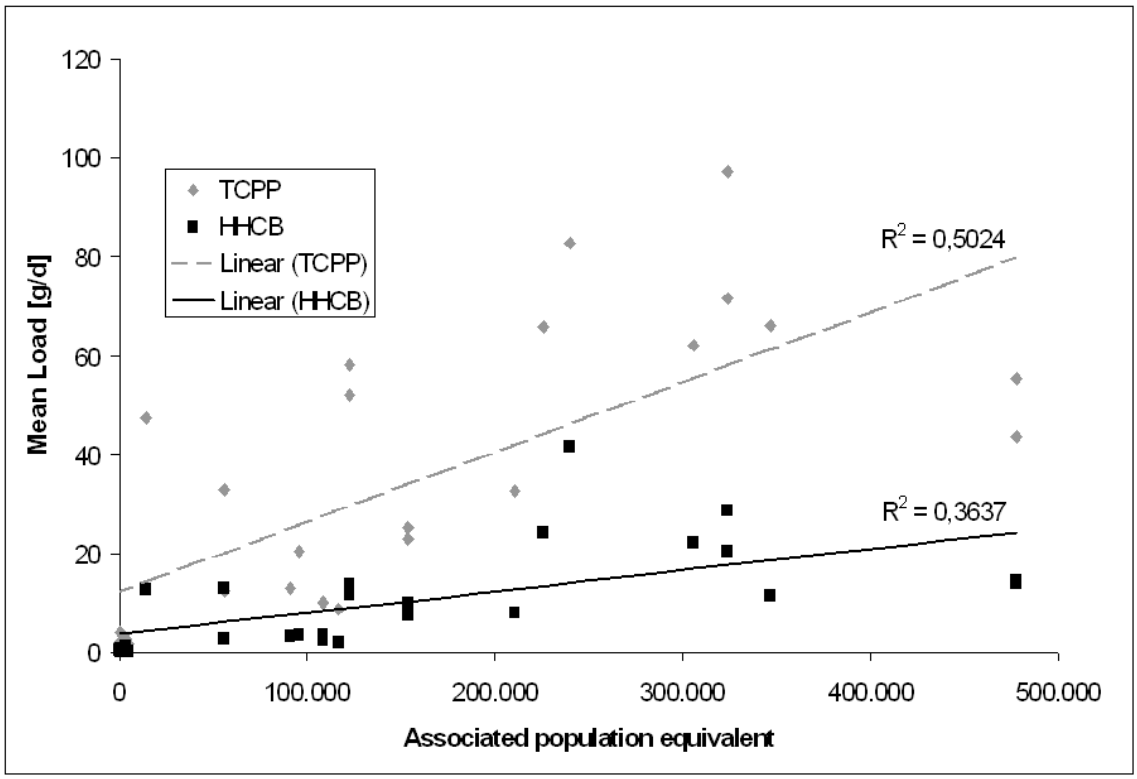


Figure 10: Correlation between transported TCPP/ HHCB load and associated population equivalent (population equivalent was calculated on data from HLUG)

A median correlation can be observed between mean loads of investigated compounds and corresponding associated population equivalent (Figure 10). For all compounds Pearson correlation coefficients lie within the range of 0.5 to 0.7 (except for TBEP with a value of R = 0.39) and therefore validate STP´s effluents as dominating source for investigated substances. Calculation and comparison of transported load per capita at each sampling point (Table 10) reveals that at some sampling locations (Mo1, Sw2, Wi2 and Wi3) the emitted amount of the target compounds is much higher compared to all other sampling locations. For example, in case of TCPP the mean emitted amount per capita and year is 235 mg. This amount is exceeded by far at two sampling locations with values of 1239 mg/cap/year (Sw2) and 1921 mg/cap/year (Wi3). Additionally, at Mo1 and Wi2 the values are slightly above the mean value (292 mg/cap/year and 385 mg/cap/year, respectively). A similar observation is recognized for the other six target compounds. Two possible reasons can be discussed for this observation. Either upstream from sampling locations Mo1, Sw2, Wi2 and Wi3 continuously operating unknown dischargers of waste water are present or the known small-scale sewage treatment plants located upstream from these sampling locations discharge

higher loads of the target compounds into the rivers compared to the other sewage treatment plants. Further investigations are necessary to clarify this.

Table 10: Load per capita of target compounds [mg/cap/year]

	sample pts.	TCPP	TCEP	TDCPP	TBP	TBEP	HHCB	AHTN
Schwarzbach	La1	132	30	19	99	31	67	27
	La2	70	17	14	42	17	18	6
	Sw1	163	34	57	181	141	20	8
	Sw2	1239	322	330	953	390	335	100
	Sw3	39	15	8	21	10	9	3
	Sw3b	162	37	49	99	56	36	11
	Sw4	152	35	42	85	45	40	14
	Sw5	33	16	4	13	6	10	4
Modau	Mo1	292	139	313	465	353	127	61
	Mo2	59	21	18	35	14	23	7
	Mo3	57	9	13	30	10	19	5
	Mo4	66	11	13	21	10	16	5
	Sa1	34	10	14	29	14	12	4
	Sa2	40	8	12	22	13	10	3
	Sa3	27	9	4	42	6	6	2
Weschnitz	We1	241	25	125	102	132	92	27
	We2	97	40	46	76	182	21	7
	We3	107	15	62	44	42	40	10
	We4	63	13	48	45	27	23	7
	We5	71	14	30	32	18	20	7
	We6	106	19	48	47	25	31	8
Winkelbach	Wi1	-	-	-	-	-	-	-
	Wi2	385	8	267	1375	475	70	63
	Wi3	1921	362	378	1516	422	331	150
	Wi4	51	7	8	25	13	13	4
	Wi5	76	10	12	19	13	13	4
	Total	**235**	**50**	**79**	**224**	**101**	**58**	**22**

4.5 Conclusions

The concentrations of the organophosphates and synthetic musk fragrances showed a notable variability with respect to space and time. Both substance groups occurred nearly ubiquitous in the rivers of the study area and therefore, represent a potential risk for the aquatic environment. The highest concentrations were observed in the Schwarzbach system, characterized by the highest proportion of waste water. STP effluents so far were identified as the dominating source for the non-chlorinated organophosphates and the synthetic musk fragrances, but also diffuse sources are eminent, especially in the case of TBP. However, at sampling points near STP effluents and close to the river's mouth, the concentrations of target compounds were elevated. Congruously, the average transported load of the target compounds

increased from the source to the mouth of the rivers with increasing waste water input indicating that the input amount exceeds the elimination capacity within these small river systems.

Furthermore, the synthetic musk fragrances showed a clear seasonal trend with significantly lower concentrations in the summer compared to the winter, which can be ascribed to more intense evaporation and photodegradation, due to solar radiation during the summer. This seasonality restricts the applicability of synthetic musk fragrances as quantitative markers for waste waters.

5 Endocrine disruptors in freshwater streams of Hesse, Germany: Changes in concentration levels in the time span from 2003 to 2005

5.1 Abstract

Four small freshwater streams in the region known as Hessisches Ried in Germany were investigated with respect to the temporal and spatial concentration variations of the endocrine disruptors bisphenol A (BPA), 4-*tert*-octylphenol (OP), and the technical isomer mixture of 4-nonylphenol (NP). Measured concentrations of the target compounds in the river water samples ranged from <20 ng/l to 1927 ng/l, <10 ng/l to 770 ng/l, and <10 ng/l to 420 ng/l for BPA, OP and NP, respectively. BPA levels were, with the exception of two samples, below the predicted no-effect concentration (PNEC) for water organisms. NP concentrations showed a significant tendency of decreasing concentrations during the sampling period. This is mainly attributed to the implementation of the European Directive 2003/53/EG, which restricts both the marketing and use of nonylphenols. Results from the analysis of additionally collected water samples from sewage treatment plant (STP) effluents indicate that the STPs cannot be the only sources for NP found in the river water.

5.2 Introduction

In the last few years, a large variety of environmental substances of either natural or synthetic origin have been mentioned to have effects on the endocrine systems of vertebrates and invertebrates (Liehr et al., 1998). Among these endocrine disrupters, steroid estrogens like the natural hormones estradiol and estrone, as well as the synthetic hormone ethinyl estradiol are supposed to contribute mainly to estrogenic activity in STP effluents and adjacent surface waters (Desbrow et al., 1998; Shen et al., 2001). In contrast, estrogenic xenobiotics like alkyphenols exhibit much less estrogenic potency than the steroids mentioned above (Routledge and Sumpter, 1997), but are able to bioaccumulate (Ahel et al., 1993) and therefore, represent an additional risk to aquatic organisms. Furthermore, common phenolic xenoestrogens, like Bisphenol A (BPA), the technical isomer mixture of 4-nonylphenol (NP) and 4-tert.-octylphenol (OP), play a major role as environmental contaminants due to their widespread application. The compounds were often found in STP effluents (Ahel et al., 2000; Bolz et al., 2001; Espejo et al., 2002; Höhne and Püttmann, 2006a) and receiving surface

waters (Céspedes et al., 2005; Derbalah et al., 2003; Fries and Püttmann, 2003b; Heemken et al., 2001; Uguz et al., 2002).

BPA is an important intermediate used for the manufacture of epoxy, polycarbonate, phenoxy, and polysulfone resins and accounts for large production volumes of about 2.8 million t/a on a global scale (Bisphenol A Global Industrie Group, 2004). First evidence of estrogenic activity of BPA was already reported by Dodds and Lawson (Dodds and Lawson, 1936; Dodds and Lawson, 1938) in the 1930s. Since then, various studies revealed the endocrine disrupting activity of BPA for vertebrates. In more recent times, Schulte-Oehlmann et al. (2001) reported endocrine effects of BPA on invertebrates such as apple snails in concentration ranges of only a few nanograms per liter. However, the evaluation of estrogenic effects of BPA on benthic/aquatic organisms remains controversial, since in other studies (Caspers, 1998) no estrogenic effects of BPA on Daphnia magnia could be observed.

In contrast, for the alkylphenols (NP and OP) the evidence of estrogenic effects on invertebrates seems generally accepted and has been documented in various studies (Oehlmann et al., 2000; Soto et al., 1991). Estrogenicity of alkylphenols generally depends on the position and branching of the alkyl groups (Routledge and Sumpter, 1997; Tabira et al., 1999). The interaction of *para*-substituted alkylphenols with estrogen receptors is intensified together with an increasing number of the carbon atoms in the alkyl side chain (Tabira et al., 1999). The common technical 4-nonylphenol (NP) is a mixture of 22 isomers (Wheeler et al., 1997), whereof about 85% are *para*-substituted (Russ et al., 2005) and therefore, exhibit estrogenic potency. Alkylphenols are transformation products of alkylphenolethoxylates (APEOs), which are used as common industrial and household detergents. Production of nonylphenolethoxylates (NPEOs) and octylphenolethoxylates (OPEOs) in Germany reached levels of up to 37,000 t/a and 2,000 t/a in 2000, respectively (Leisewitz et al., 2001b). More than 20 years ago, APEOs became a subject of public discussion due to supposed toxicity. As a consequence, in 1986 APEO-manufacturing industries in Germany decided, as kind of a self-commitment, to substitute the application of APEOs in household and later also in industrial detergents. Since that time, a significant decrease of NP concentration levels within sewage sludge (Jobst, 1998) and surface waters (Leisewitz and Schwarz, 1997) have been recorded. However, the amount of NP remained at a high level in STP effluents from Germany in the late 1990s (Hegemann et al., 2002) and in receiving waters in early 2000 (Fries and Püttmann, 2003b). In the last few years, the European Union has subjected NP to the risk assessment procedure, and furthermore, added the substance to the list of priority substances of the EU Water Framework Directive 2000/60/EC. Also, BPA and OP are

regarded as substances of environmental concern and are therefore currently passing the risk assessment procedure according to the Council Regulation (EEC) No 793/93 on the evaluation and control of the risks of existing substances.

Therefore, further analyses regarding the development of concentration levels of endocrine disruptors in rivers are still required. The present study provides monitoring results of endocrine disrupting substances such as BPA, OP, NP in small freshwater streams in Hessisches Ried (South Hesse, Germany) in the time span from September 2003 to September 2005.

5.3 Methods and Materials

5.3.1 Chemicals

Chemical standard substances were purchased from Ehrenstorfer (NP) and Sigma Aldrich (OP and BPA).

5.3.2 Sampling

Sampling of river water took place in a region south of Frankfurt am Main, Germany called Hessisches Ried. The region is densely populated and industrialized and drained by four small river systems: Schwarzbach, Modau, Winkelbach, and Weschnitz (from north to south), which are tributaries to the Rhine River. These river systems discharge only small water volumes, ranging from 0.3 m³/s (Winkelbach) to approx. 3 m³/s (Weschnitz) of water on an annual basis. The rivers serve as receiving waters for large amounts of treated wastewater, leading to nearly 100% wastewater contents during extremely dry periods (Göbel, 1996). The rivers' courses emanate from artificial drainage measures in the former Rhine River floodplain about one hundred years ago. The whole area is crisscrossed by more or less actively used draining channels leading to a very complex hydrological discharge system, which is also influenced by further human activities, such as flood control and artificial groundwater recharge. At the lower reaches, all rivers are diked and river beds were largely converted to artificial trapeze profiles.

A total of 227 water samples were collected from the four river systems in the time span from September 2003 to September 2005. The sampling surveys were carried out at intervals of 2 to 4 months. A volume of 2.5 l of surface water was collected on each of the 26 sampling

points. Simultaneously, some parameters like water temperature, conductivity, and pH-value were recorded at each sampling point. Additionally, during the summer of 2005, four STP effluents were included in the sampling survey to assess the influence of wastewater input on the concentrations of target compounds in the rivers. In total, 28 STPs of different sizes discharge into the rivers of the sampling area, thereof two major size (Darmstadt and Weinheim) and two mid-size STPs (Da/Eberstadt and Pfungstadt) were selected for sampling in June and September 2005. Geographical positions of all sampling points, including surface water and STP effluents, can be obtained from Figure 2. All water samples were stored in brown glass bottles and kept cool (at 4°C) during transport to the laboratory where they were processed the day after sampling campaign.

5.3.3 Sample preparation and analysis

Samples were extracted by solid phase extraction (SPE) and afterwards analyzed by coupled gas chromatography/mass spectrometry (GC/MS). Before extraction, samples had to pass through pre-cleaned paper filters (597½, Schleicher & Schuell) to remove coarse particles and suspended solids. SPE was carried out using Bond Elute PPL (Varian, 1 ml) cartridges. SPE cartridges were eluted three times with 333 µl of methanol/acetonitrile mixture (50:50). Extracts were then dried in nitrogen stream, resolved in 100 µl acetonitrile, and 4,000 ng of squalane was added as internal standard to each extract. The samples were analyzed using a Fisons gas chromatograph GC 8000 coupled to a Fisons MD 800 mass spectrometer. The gas chromatograph was equipped with a BP-X5 capillary column (30 m length, 0.25 mm inner diameter and 0.25 µm film thickness). Helium was used as carrier gas. The temperature program of the GC oven operated from 80°C to 300°C with a rate of 4°C per minute. Sample injection (1 µl) was carried out in splitless mode. The mass spectrometer used electron ionization (EI, 70eV) and was operated in full-scan mode (50 – 600 m/z).

The target compounds BPA, OP, and NP were identified by mass spectra and retention time (Table 11). Quantification of target compounds was based on the internal standard method and was performed as described in Fries and Püttmann (2003b) and Höhne and Püttmann (2006a). Limits of detection (LOD) using this method were 10 ng/l for OP and NP and 20 ng/l in the case of BPA.

Table 11: Analytical parameters of BPA, OP and NP

	ions used for identification	ions used for quantification	detection limit [ng/l]	recovery rate [%]
BPA	213, 228	213	20	86
4-*tert*-octylphenol	107, 135, 206	135	10	107
tech. 4-nonylphenol			10	90
isomer group 1 (*m/z* 177)	107, 121, 149, 163, 177, 220	177	10	90
isomer group 2 (*m/z* 149)	107, 121, 149, 191, 220	149		
isomer group 3 (*m/z* 135)	107, 135, 220	135		
isomer group 4 (*m/z* 121)	107, 121, 163, 177, 220	121		

5.4 Results and Discussion

5.4.1 Flow conditions of the rivers

Flow conditions of the rivers during the sampling period were not stable, but subject to seasonal fluctuations and dependent on the river system (Figure 11). Weschnitz and Modau showed high discharge in October 2004 and April 2005, and low discharge in September 2005. Schwarzbach is characterized by a different flow regime showing the discharge maximum in December 2004 and discharge minimum in June 2004 and June 2005. The Winkelbach, the smallest river of those sampled, shows the lowest discharge variation with only two remarkable events: maximum in April 2005 and minimum in June 2005. However, due to the combined treatment of urban runoff and sewage water in the treatment plants, higher discharge in these small rivers is often accompanied by higher wastewater input. Hence, no significant correlation between concentration of the target compounds and water discharge could be established.

In general, electrical conductivity is an adequate parameter to survey water purity since sewage treatment as well as agricultural runoff increases the amount of total dissolved solids. However, the correlation of NP and OP with electrical conductivity ($r = 0.2$ and significant at the 0.01 level, 2-tailed) is low. Simultaneous measured electrical conductivity at sampling points indicates that only the high flow event in April 2005 can be regarded as a real dilution event (possibly caused by snow melt at the upper reaches).

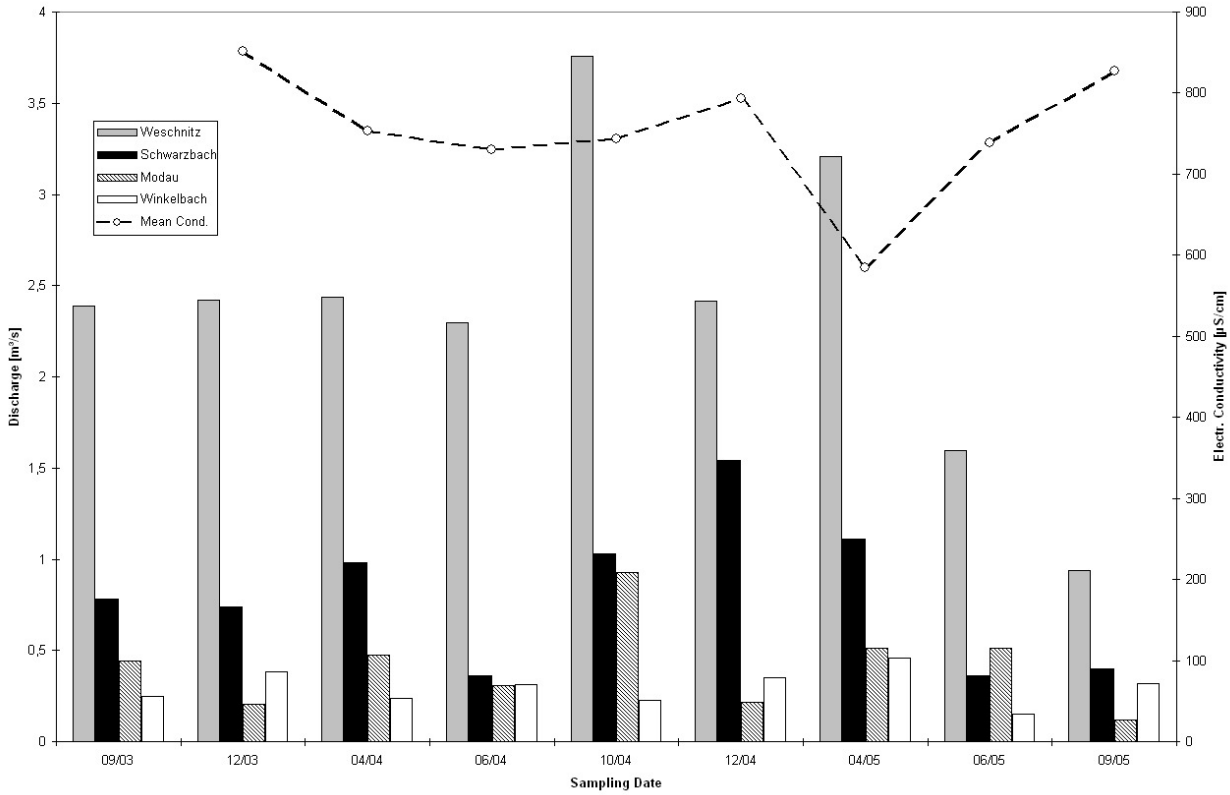


Figure 11: Flow conditions and mean electrical conductivity of sampled rivers during the sampling period

5.4.2 Technical 4-nonylphenol (NP)

In the time span from September 2003 to September 2005, a total of 227 river water samples were collected. The results of the analyses are presented in Table 12.

Table 12: Concentrations of endocrine disruptors BPA, OP and NP [ng/l] in surface water samples from Hessisches Ried in the time span from September 2003 to September 2005

		NP	OP	BPA
N	**Valid**	227	227	227
	< LOD	126	71	197
Minimum		< 10	< 10	< 20
Maximum		770	420	1924
Std. Deviation		145	51	259
Mean		**57**	**40**	**57**
Median		< LOD	30	< LOD

NP was detected in about 44% of the water samples showing concentrations between <10 ng/l and 770 ng/l. At two sampling surveys, (April 2005 and June 2005) NP was actually not detectable at all in the water samples (Figure 12). These concentrations are within the range of previously reported values obtained in the year 2000 from the Elbe River and its tributaries

ranging from 13 ng/l to 53 ng/l for NP (Stachel et al., 2003). In smaller rivers, comparable to those sampled in the present investigation, NP concentrations ranging from < LOD to 485 ng/l were measured (Bolz et al., 2001). Former monitoring data of NP in the sampling area of the late 1990s could only prove the presence of NP within the rivers of the Hessisches Ried, but are quantitatively not confidential due to analytical problems and diverging limits of quantification (Fengler et al., 2002).

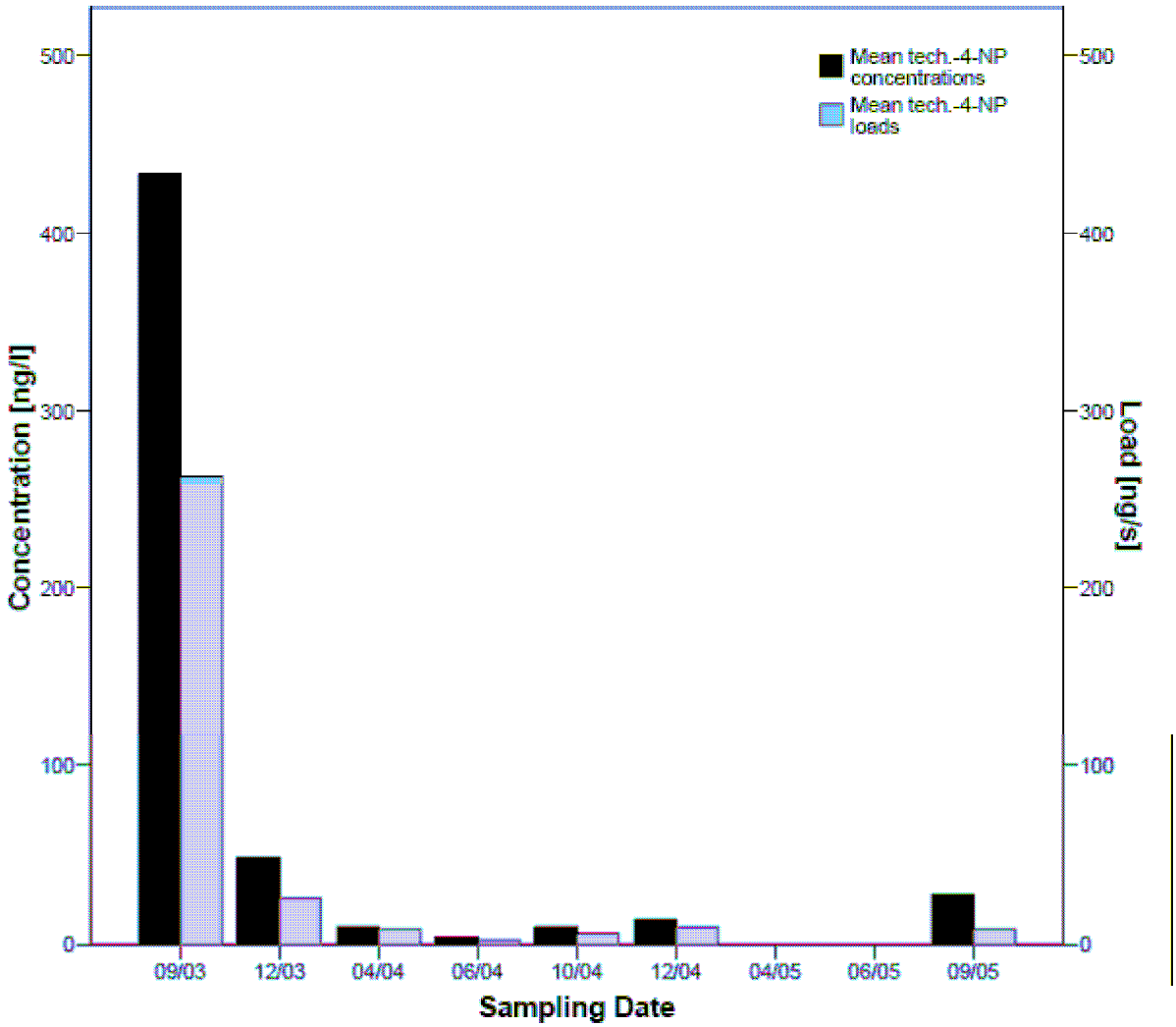


Figure 12: Development of NP concentrations and load during the sampling period from Sept 03 to Sept 05

The bulk (93%) of measured NP concentrations are beneath the predicted no effect concentration (PNEC) for water at 330 ng/l, which should be protective for toxic effects of algae and estrogenic effects in fish according to the European Risk assessment. In September 2003, the concentrations exceeded PNEC in 16 samples, but were about one order of

magnitude lower than the concentrations of 10-20 µg/l expected to cause estrogenic effects (ECB, 2002). Later on, no higher concentrations at any sampling date were detected.

Measured concentrations of NP were highest in September 2003, revealing a mean concentration of 433 ng/l and decreased since that time to a significantly lower level of about 30 ng/l in September 2005. This cannot be explained by discharge variations alone, since water discharge in September 2003 was at an average level, and calculated loads of NP tend to decrease since that time (Figure 12). This indicates a significant decrease of the input of NP into the river systems of Hessisches Ried. These findings coincide with the results from the analysis of influents and effluents from sewage treatment plants (Höhne and Püttmann, 2006a). A similar tendency of decreasing NP concentrations has also been observed in wastewaters and river waters in Switzerland (Voutsa et al., 2006). This observed decrease of NP concentrations in influents and effluents of sewage treatment plants can be explained by the implementation of the European Directive 2003/53/EG. According to this directive, usage of NP and the related ethoxylates NPEOs as industrial or commercial cleaning agents has been prohibited since January 2005. This prohibition was expected since the EU added nonylphenol and nonylphenolethoxylates to the list of priority substances in November 2001. The analytical results suggest that the industries involved may have adapted their operating processes to the new restrictions prior to the year 2004, so that positive effects in surface and waste waters were already noticeable at the beginning of 2004.

Analyses of STP effluent samples from the sampling area in June and September 2005 revealed results that are comparable to those reported previously by Höhne and Püttmann (2006a). In only one effluent sample out of eight, NP was detected at only 11 ng/l, which is slightly above the detection limit (Table 13). Despite the absence of remarkable STP wastewater inputs of NP, mean concentrations of 30 ng/l NP were found in September 2005 within the river systems. This indicates the presence of additional sources of NP within the river. Heemken et al. (2001) pointed out that alkylphenols tend to enrich in the particulate matter of freshly deposed sediments. Moreover, Isobe et al. (2001) found 20% of the NP to be present within the particulate phase and documented the strong affinity of NP to suspended particulate matter. Furthermore, they suggested in-situ production of alkylphenols from ethoxylates in river sediments. In several studies high amounts of NP in river sediments have been reported (Bolz et al., 2001; Croce et al., 2003; Heemken et al., 2001; Isobe et al., 2001; Li et al., 2004). Li et al. (2004) found a reasonable correlation between the concentration of NP in water and in suspended matter, leading to a partition coefficient logKp of 4.8 between suspended and dissolved phases. Therefore, in absence of direct input of NP by wastewater, a

redissolution of NP from the sediment or deposited suspended matter seems conceivable. However, due to several artificial barrages within the rivers' courses, sediment dynamics are rather indeterminate.

Table 13: Concentrations of BPA, OP and NP [ng/l] disruptors in STP effluents in June and September 2005

	BPA [ng/l]		OP [ng/l]		NP [ng/l]	
	June 05	*Sept 05*	*June 05*	*Sept 05*	*June 05*	*Sept 05*
STP Da-Eberstadt	< LOD	< LOD	< LOD	72	< LOD	< LOD
STP Darmstadt	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
STP Pfungstadt	< LOD	< LOD	< LOD	19	< LOD	< LOD
STP Weinheim	< LOD	< LOD	333	82	< LOD	11

In addition, some other diffuse sources also have to be taken into account. For example, NP still serves as an emulgating agent in some pesticides (Guenther et al., 2002) and therefore, NP might enter the surface waters via field runoff in agricultural areas like the sampling region. Furthermore, leaching of NP from land-applied sewage sludge (La Guardia et al., 2001) and from agriculture polluted soil (where direct spillage of biocides was suggested) into groundwater (Latorre et al., 2003) has been reported and cannot be completely excluded. However, these are diffuse sources and are very difficult to link to measured NP-concentrations on the basis of the available data sets.

5.4.3 4-*tert*-octylphenol (OP)

Unlike 4-nonylphenol, 4-tert.-octylphenol showed a widespread occurrence in the study area and was detected in over two thirds of the analyzed water samples. Measured concentration levels ranged from <10 ng/l to 420 ng/l, representing highest concentrations in September 2003 and lowest concentrations in April 2005. The latter can be explained by dilution effects within the rivers due to stronger seasonal rain and snowmelt water entries. In Figure 13, seasonal variation of OP concentrations as well as seasonal changes in conductivity are presented, assuming that low conductivity in April 2005 with only about 600 µS/cm results from the aforementioned dilution effect. In contrast, high water discharge in October and December 2004 did not lead to lower OP concentrations, which remained in the same order of magnitude or increased slightly compared to the other sampling dates. In about 9% of all water samples, the measured OP concentrations exceeded the PNEC for water at 100 ng/l,

which was introduced by the German Federal Environmental Agency because of toxicity of OP to aquatic organisms (Rüdel et al., 2001). With the exception of September 2005, this value was exceeded in at least one sample within each sampling period.

The median concentration of OP within the analyzed river systems accounts for about 30 ng/l and indicates a slight decrease since September 2003. The concentration levels are within the range of values reported recently from German and Austrian rivers. Bolz et al. (2001) found OP concentrations of up to 163 ng/l and a median concentration of 31.4 ng/l in the Körsch, a small freshwater stream in southern Germany. In Austrian rivers, concentrations of OP ranging from <5 to 88 ng/l have been reported (Scheffknecht, 2005). For larger rivers like the Rhine and the Elbe River, concentrations of 130 ng/l (RIWA-Secretariat et al., 2005) and 0.5 to 3.3 ng/l (Stachel et al., 2003) respectively were published.

STP effluents are considered to be a major source for OP in rivers, and a recent investigation on Hessian STPs effluents (Höhne and Püttmann, 2006a) yielded median effluent concentrations of 38 ng/l and maximum concentrations of 392 ng/l. These values reflect the same dimension that we found within the rivers and moreover, coincide with our findings on STP effluents discharging into the sampling area, where we detected OP in four out of eight samples, accounting for up to 333 ng/l.

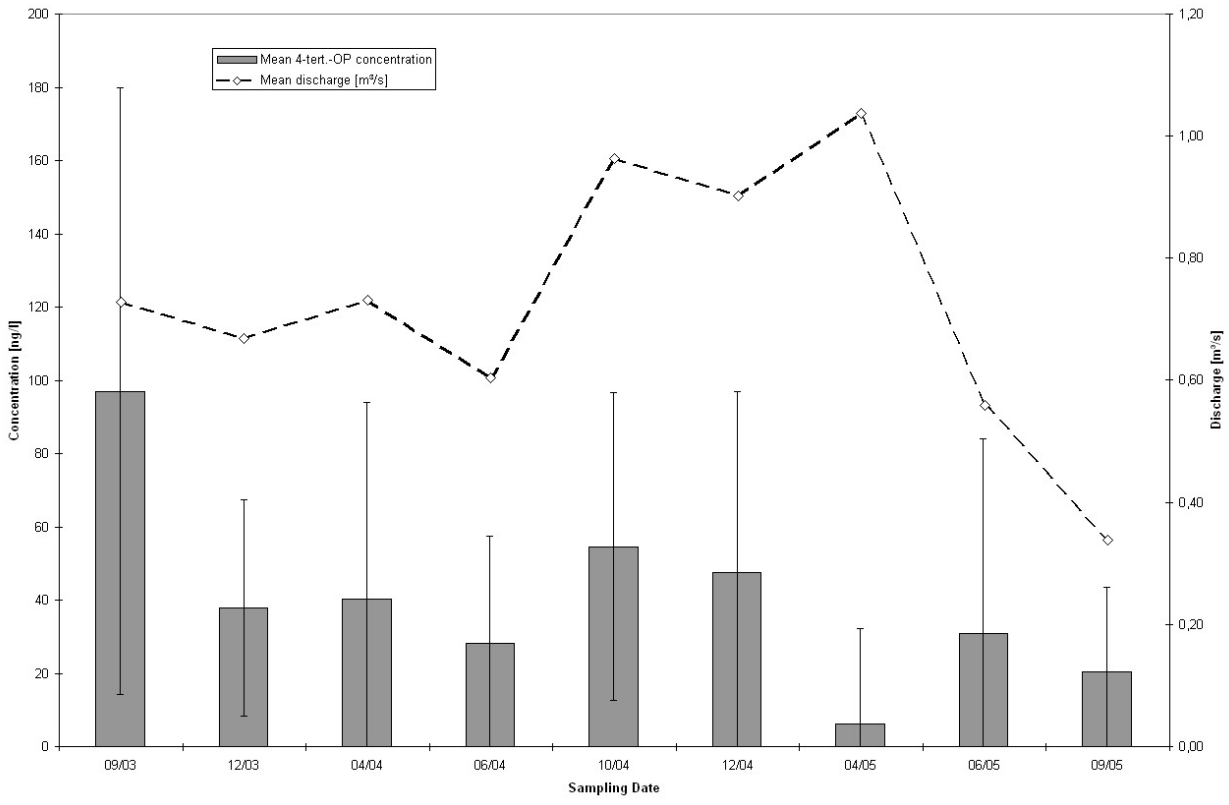


Figure 13: Development of OP concentrations during the sampling period from Sept 03 to Sept 05

Besides sources for OP, there are also sinks within the river. For instance, like NP, OP tends to bond to the sediment which represents an important mechanism for removal of OP from surface waters (Johnson et al., 1998). According to Johnson et al. (2000), OP is not biodegradable in anaerobe sediments and therefore tends to accumulate under such conditions. In the same study, Johnson et al. observed biodegradation of OP within the water phase and found half-lives varying between seven and 50 days, with degradation velocity showing temporal and spatial differences. With respect to the rivers investigated in the present study, at mean flow velocity of 0.4 m/s and maximal flow distances of 30 km to the river's mouth, biodegradation can be expected to be limited and OP will preferentially be exported to the Rhine River, if not bound to the sediment or degradated photochemically (Ahel et al., 1994b).

5.4.4 Bisphenol A (BPA)

BPA was far less evident than the tested alkylphenols and could be found in only 30 out of 227 samples, with most of them (19) detected in samples from October 2004. In December 2003 and from April 2005 until the end of the sampling period in September 2005, no BPA was detected whatsoever (Figure 14). The measured concentrations of BPA were very high, ranging from the detection limit of <20 ng/l up to 1.924 ng/l. In 20 % of the samples where BPA was detected, concentrations exceeded 1 µg/l. Furthermore, at two sampling points in September 2003, the measured BPA concentrations even exceeded the predicted no-effect concentrations (PNEC) for water organisms at 1.6 µg/l (ECB, 2003), proposed by the European Chemical Bureau. Recent studies mainly report lower values for BPA concentrations in German and Austrian rivers (<LOD to 272 ng/l (Bolz et al., 2001) and <5 to 260 ng/l (Scheffknecht, 2005), respectively), but high concentrations were also found in Thuringian rivers (Stachel et al., 2003) (up to 4,400 ng/l in the Pleiße River) and were primarily attributed to upstream-located STP inputs. BPA is easily biodegradable (Staples et al., 1998) and therefore largely eliminated in STPs, but has nevertheless been detected occasionally within the effluents. In a recent study, Höhne and Püttmann (2006a) reported effluent concentrations of up to 7,625 ng/l BPA in Hessian STP effluents, but detection frequency was rather low (it was detected in only about 15% of the samples). Data obtained in the present study from STP effluents within the sampling area during June and September 2005 is consistent with these findings, yielding no BPA within the sampled STP effluents at that time, whereas in concomitant river samples, no BPA could be detected either. Finally, we assume that detected high BPA levels within the sampled rivers can be attributed to

occasional BPA inputs by STPs, but will be rapidly eliminated in the water due to its good biodegradability. Consistent with these findings, Dorn (1987) specified half-live times of BPA within rivers of 2.5 to 4 days. Despite the rather high water solubility of BPA (120–300 mg/l (Bisphenol A Global Industry Group, 2004)), the compound tends to adsorb to the sediment (Stachel et al., 2003) and has been detected therein (Fromme et al., 2002; Heemken et al., 2001). Therefore, sorption to sediments could be another possible sink for BPA within the river. However, due to its lower logKow, this effect is supposed to be less evident compared to the alkylphenols' coefficients.

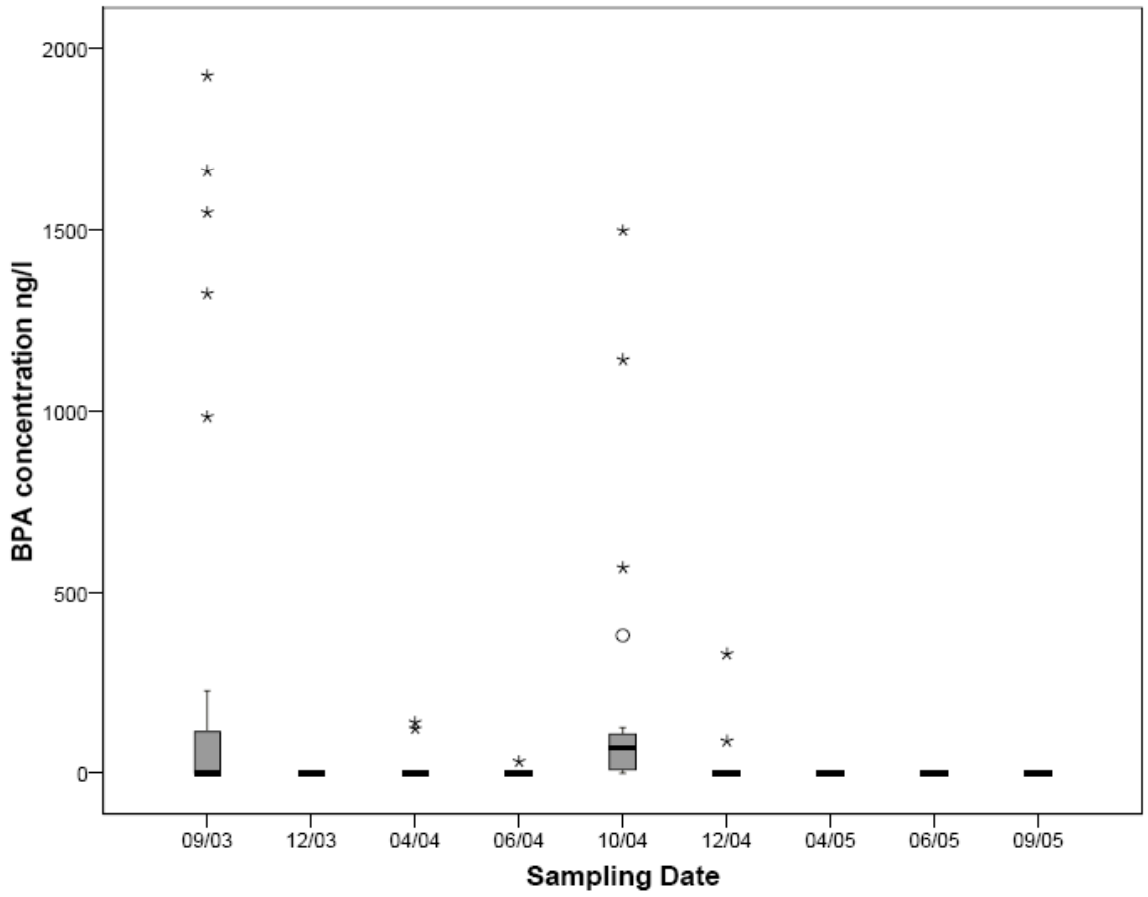


Figure 14: Development of BPA concentrations during the sampling period from Sept 03 to Sept 05

5.5 Conclusions

Endocrine disruptors BPA, OP, and the technical isomer mixture of 4-nonylphenol (NP) were analyzed in 227 water samples of freshwater streams in the Hessisches Ried, collected in the time span from September 2003 to September 2005. While OP was detected in 69 % of the water samples, NP and BPA were far less abundant. Measured alkylphenol concentrations in some samples exceeded the PNEC values for water, but were generally below the limit where

alkylphenols are suggested to have endocrine effects. In case of NP, concentrations exceeding the PNEC values were only found in September 2003.

Moreover, a significant decrease of NP concentrations in the sampled rivers from September 2003 (median NP concentration of 426 ng/l) to September 2005 (median NP concentration of 25 ng/l) was detected. A possible explanation might be the implementation of the European Directive 2003/53/EG and associated application ban for NP and NPEO in many products. Furthermore, the absence of NP in discharging STP effluents in the sampling area reveals the existence of other input or in-situ sources for NP in the river water. Redissolving from sediments and contaminated field run-off in agricultural areas can be considered as possible sources.

BPA could be found occasionally (only in 13% of all samples) in the water samples, but in these samples at very high concentrations, exceeding in two cases the predicted no-effect concentration for water organisms at 1.6 µg/l (2003). Therefore, adverse effects on aquatic organisms throughout endocrine disruption cannot be excluded.

6 Monitoring terbutryn pollution in small rivers of Hesse, Germany

6.1 Abstract

Four small river systems in Hesse, Germany, were investigated with respect to seasonal and spatial concentrations of the herbicide terbutryn [2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine]. Despite introduction of a ban on its use as a herbicide in July 2003, terbutryn was still present in the rivers during the whole sampling period from September 2003 to September 2006, and there was no trend of decreasing concentration during this time. In the Weschnitz and Modau river systems the mean terbutryn concentration exceeded the German drinking water ordinance threshold value for single biocides. Maximum concentrations of up to 5.6 µg/l were determined in the Weschnitz River. Higher terbutryn concentrations in summer are suggested to originate from agricultural sources as well as from sediment redissolution. Effluents of two sewage treatment plants had high terbutryn concentrations, indicating that terbutryn enters the rivers from this source. Sources other than agriculture must explain terbutryn occurrence in the rivers during winter, when farm pesticide application typically ceases. The potential for mobilization of terbutryn from sediments and leaching from soils are discussed.

6.2 Introduction

Terbutryn [2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine] belongs to the group of triazine herbicides. Triazines inhibit photosynthesis by interrupting the electron transport system (Steinback et al., 1981), and are powerful tools for weed control in agriculture. Terbutryn is an active ingredient in many past and current plant protection products including Segard®, Opogard®, Topogard 50®, Terbutrex 80 WDG®, Terbutrex FW®, Amigan®, Logran Extra®, Hora-Terbutryn®, Hora-Tryn 500®, Fali Terbutryn 500®, Igran® and Zera-Terbutryn®. These herbicides are still preferentially applied in maize, pea and cereal culture. In accordance with the European Council Directive 91/414/EEC and the European Commission Regulation (EC) 2076/2002, authorization of plant protection products containing terbutryn was withdrawn on 25 July 2003, although a period of grace that expired on 31 December of 2003 was allowed. Since that date, the use of such products in agriculture

has been strictly forbidden in the European Union, with the exception for the UK, Spain, Ireland and Slovakia, where authorization is due to expire not later than 31 December 2007.

In Germany most of the triazine herbicides were banned during the last decade (atrazine 1991, simazine 2000) because of their persistence in aquifers and the resulting threat to drinking water resources. Terbutryn was one of the last triazine compounds for which authorization for use as a herbicide was revoked. It is evident that a ban on use does not necessarily lead to immediate disappearance of the banned substance from the environment. In Germany atrazine was still detected in 1997 (Nitschke and Schussler, 1998) in effluents of sewage treatment plants (STPs), and until recently was found as a diffuse contaminant in groundwater (Tappe et al., 2002). The use of atrazine in France was banned in September 2003, but the concentration of atrazine and its metabolite desethylatrazine in groundwater of an agricultural catchment has not subsequently decreased significantly (Baran et al., 2007; Barth et al., 2007). In Belgium the agricultural use of atrazine was only banned in 2005. At that time high concentrations (up to 0.736 µg/l) of the herbicide were found in water of the Scheldt Estuary (Belgium/Netherlands) (Noppe et al., 2007). A recent study showed that some agricultural merchants in Germany were selling pesticides that are prohibited in Germany but still allowed in other European countries (Greenpeace, 2006).

In addition to illegal application of terbutryn as an agricultural herbicide, there are several legal uses of products containing terbutryn that enable this substance to enter the aquatic environment. For instance, terbutryn is used as an aquatic herbicide for control of algae in garden ponds and indoor aquaria, and as a biocide in antifouling paints and coatings. A recent study of roof paints (Menge, 2005) showed leaching of terbutryn and other herbicides from treated materials, and estimated terbutryn concentrations up to 2 mg/l in roof water run-off. Terbutryn is slightly toxic to humans, but has been shown to have moderate toxicity to aquatic organisms including algae (EbC50 – 72 h) at concentrations of 2 µg/l (Okamura et al., 2000) and *Daphnia magna* (EhC50 – 48 h) at 7.1 mg/l (Marchini et al., 1988).

Terbutryn has been detected in rivers (Carabias-Martinez et al., 2003; Garmouma et al., 1998), coastal waters of the Mediterranean Sea (Tolosa et al., 1996), marine sediments of the North Sea (Bester and Huhnerfuss, 1996), and in groundwater dwells of agricultural areas in Spain (Carabias-Martinez et al., 2003) . In Germany terbutryn has recently been detected in the Elbe (UBA, 2004) and Wupper (LUA-NRW, 2002) rivers at concentrations of 0.003 µg/l and 0.064 µg/l, respectively. These concentrations are low, but the German water quality objective for terbutryn in surface waters (which results from implementation of the EU water framework directive and the objective of achieving a “good ecological status”) is only

0.03 µg/l. Thus, further monitoring to identify affected regions and possible sources of terbutryn is required.

6.3 Methods and Materials

6.3.1 Study area and sampling

The study area was in the Hessisches Ried region (near Frankfort, Hesse, Germany). This is an agricultural area drained by four small rivers (the Schwarzbach, Modau, Winkelbach and Weschnitz River), all of which are tributaries to the Rhine River and serve as receiving waters for treated wastewater (river characteristics are shown in Table 1). Water samples were collected from various sampling sites associated with these rivers and analyzed for the presence of terbutryn. Figure 2 provides an overview of the sampling locations and the geographical position of STPs in the sampling area.

The Schwarzbach and Weschnitz River receive the greatest volume of treated wastewater, but due to the larger volume of the Weschnitz River the proportion of wastewater in the flow at its mouth is lowest. In contrast, the Winkelbach River has a low total discharge (only about 0.3 m³/s) and input from only a few STPs, but has a relatively high wastewater proportion (about 47 %) in the flow at its mouth. Some sampling sites had no wastewater influence (Wi1) but at others (e.g. La1) the wastewater content was almost one hundred percent. The Weschnitz River was sampled at six sites (We1–We6). Between We1 and We3 the river is split into the so called 'old' and 'new' Weschnitz River, with We2 on the old river and We3 on the new. The Weinheim sewage treatment plant discharges only into the new Weschnitz River. The Winkelbach River was sampled at five sites. Only small STPs discharge between sampling locations Wi1 and Wi3. Downstream of Wi3 the input of sewage effluent increases significantly due to discharge from a large treatment plant (90,000 population equivalents) located at Lindenbruchgraben. The Modau–Sandbach system was sampled at 7 sites. Downstream from the Eberstadt STP the Modau River splits into the Sandbach and Modau rivers, and both join the Rhine River near Stockstadt. Three sampling sites were situated on the Sandbach River (Sa–Sa3) and four were situated on the Modau River (Mo1–Mo4). In the northern part of the study area a complex system of creeks and ditches discharge surface and sewage water, with the Schwarzbach and Landgraben rivers being the dominant part of the discharge system. The Landgraben River discharges into the Schwarzbach River about 6 km from the entry of the latter into the Rhine River. The Schwarzbach and Landgraben rivers

were sampled at six sites (Sw1−Sw5) and two (La1−La2) sites, respectively. Two STPs were sampled in this area (Darmstadt and Nauheim).

Samples were collected on 13 occasions from 26 sampling sites between September 2003 and September 2006. Parameters including water temperature, conductivity and pH were recorded at each sampling site on each occasion. Additionally, during the summer of 2005 the effluents from four STPs were sampled to assess the influence of wastewater input on the concentrations of the target compound in the rivers. Actual discharge volumes were determined from the flow profiles and flow velocities. Flow velocities were determined using a hydrometric vane from OTT Messtechnik (Kempten, Germany). Water samples were collected from the middle of each river in 2.5 l brown glass bottles, and stored at 4°C until processed in the laboratory.

6.3.2 Sample preparation and analysis

Samples were passed through pre-extracted paper filters (Schleicher & Schuell, grade 597½) and then extracted by passage at low pressure (approximately 800 mbar) through solid phase extraction (SPE) cartridges (Bond Elut, 1 ml). Prior to use the cartridges were rinsed with 1 ml methanol and then conditioned with 1 ml methanol/acetonitrile (50:50) and 1 ml distilled water. The cartridges were dried with high purity nitrogen, and then eluted with 1 ml methanol/acetonitrile (50:50). The extracts were dried under nitrogen and then dissolved in 100 µl acetonitrile. The extracts, containing added squalane (4 µg) as an internal standard, were subjected to GC-MS analysis using a Fisons GC 800 gas chromatograph equipped with a BP-X5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness). Helium was used as the carrier gas. The oven temperature program started at 80°C and was raised to 300°C at the rate of 4°C per minute. Extracts (1 µl) were injected in split less mode. The mass spectrometer (Fisons MD 800) used electron ionization (EI, 70 eV) and was operated in full-scan mode (50−600 m/z).

Terbutryn as single pesticide standard and Pesticide Mix 12 (to verify the method for other common triazines) were purchased from Ehrenstorfer (Augsburg, Germany) and included in the analyses. Terbutryn and further triazines were identified by GC-MS spectrum library. Figure 15 shows the chromatogram of a triazine standard containing prometon, atrazine, propazine, ametryn, prometryn and terbutryn.

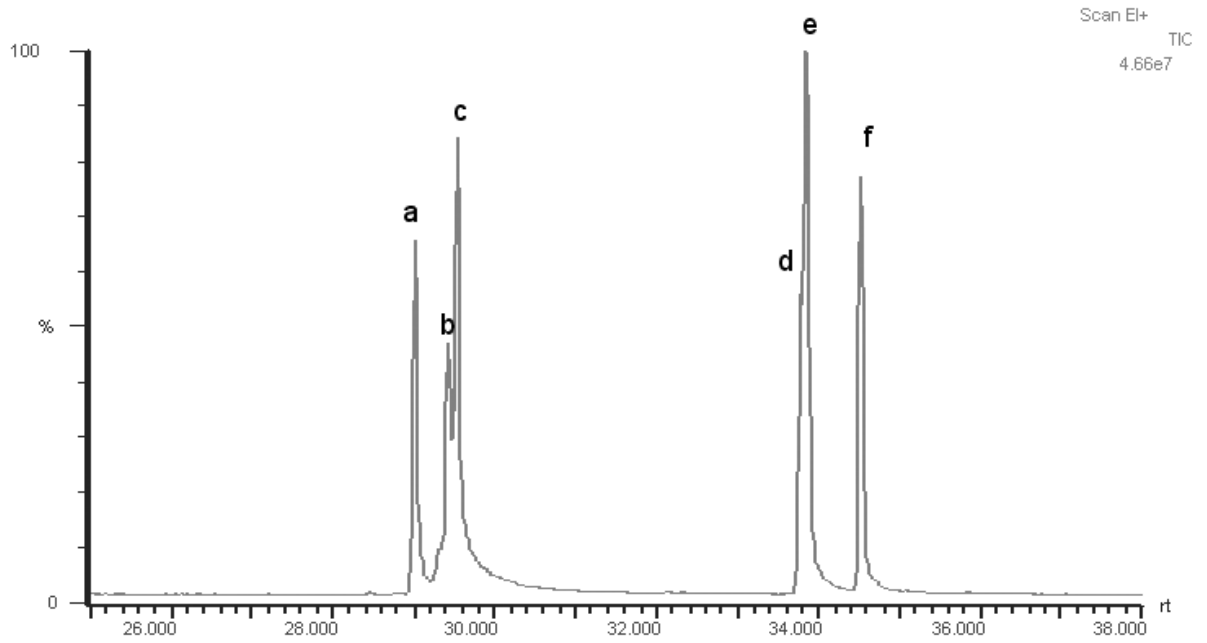


Figure 15: Total Ion Chromatogramm (TIC) of some analyzed triazines: a) prometon b) atrazine c) propazine d) ametryn e) prometryn f) terbutryn

The mass spectra of terbutryn obtained by GC/MS analysis of a river water sample is displayed in Figure 16. Quantification of terbutryn was performed using the mass trace m/z = 226 (quantifier ion). Detection and quantification limits were determined in accordance with DIN 32 645 (1994) and were 0.004 µg/l and 0.013 µg/l, respectively. For the calibration, standard solutions of terbutryn were prepared at 2 µg/l, 1µg/l, 0.2 µg/l, 0.1 µg/l, 0.05 µg/l, 0.02 µg/l, 0.005 µg/l, 0.002 µg/l and 0.001 µg/l. Recoveries were between 72 % and 89 %. Standard variation was below 10 % up to a terbutryn concentration level of 0.05 µg/l. Because of low detection frequency of the tested triazines in the water samples calibration and quantification was only carried out for terbutryn.

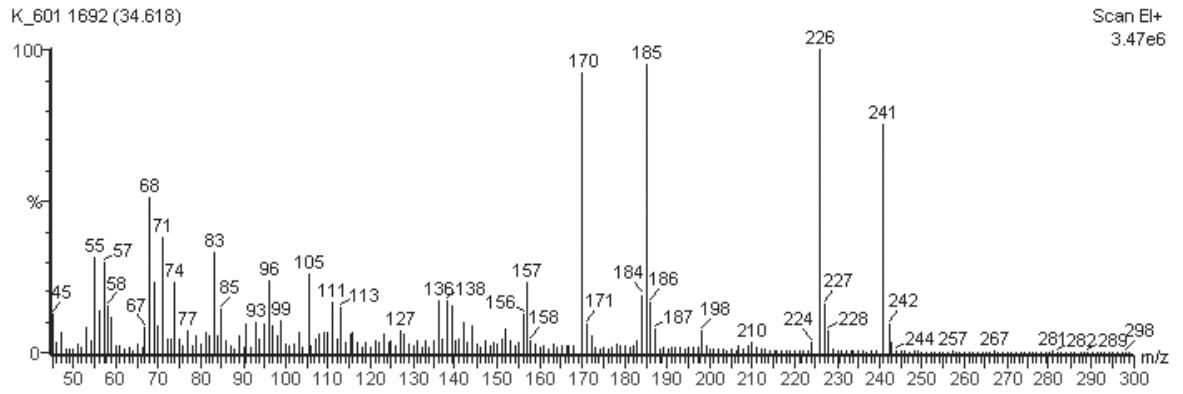


Figure 16: EI+ Mass spectrum of terbutyn obtained by GC/MS analysis of a water extract from Weschnitz river

6.4 Results

Terbutryn was found in 282 of 330 samples, and results indicated the presence of the compound in all rivers throughout the whole year. The highest concentration of terbutryn (5.6 µg/l) was measured at site We3 on the Weschnitz River in June 2004. The German Drinking Water Ordinance (TVO) threshold value for individual pesticides is 0.1 µg/l, and this value was exceeded in more than half (157) of the analyzed samples. This is remarkable since parts of the Hessisches Ried region are declared drinking water protection areas, and infiltration of terbutryn from surface water to groundwater has to be considered. The German working group on water issues (LAWA) has recently proposed an annual mean threshold value of 0.03 µg/l terbutryn, toward achieving a "good ecological status" for river water under the European water framework directive. This threshold value was not exceeded at the six sampling sites located distant from STPs in the rivers. At all other sampling locations, and particularly at most of the sampling sites on the Weschnitz and Modau Rivers, the mean concentration (four measurements in one year) exceeded the threshold value. The mean concentrations of terbutryn in the Modau and Weschnitz rivers were 0.58 µg/l and 0.54 µg/l, respectively, but in the Winkelbach and Schwarzbach rivers the concentrations were significantly lower (at least one order of magnitude, Table 14).

Table 14: Mean terbutryn concentration in the sampled river systems

Rivers	Number of samples	Min [µg/l]	Mean [µg/l]	Max [µg/l]
Schwarzbach	99	< 0.004	0.06	0.25
Modau	89	< 0.004	0.58	3.07
Winkelbach	65	< 0.004	0.03	0.55
Weschnitz	77	< 0.004	0.54	5.60

Other herbicides of the triazine group, such as prometon, atrazine, propazine, ametryn, prometryn, terbutylazine, sebuthylazine and cyanazine were not detected in the water samples. An experiment using these triazines as a standard solution confirmed the suitability of the SPE method for analysis of these herbicides in water samples. In the water samples from Hessisches Ried these triazines were detected only occasionally, at concentrations not exceeding the reference value of 0.1 µg/l.

6.4.1 Spatial variations of terbutryn in the Hessisches Ried catchment area

A major input of terbutryn to the Weschnitz River between sampling points We1 and We3 over the whole sampling period was indicated by an increase in average concentration from below the quantification limit to 1.2 µg/l. One explanation is that site We3 was only 4 km downstream from the Weinheim STP effluent discharge into the river. This plant treats approximately 12.5 million m³ of sewage originating from about 180,000 inhabitants in an area supporting intensive agriculture activity (M. Reichelt 2005, personal communication). Spot sampling of the STP effluent in June and September 2005 revealed terbutryn concentrations of 2.5 µg/l and 1.7 µg/l, respectively (Table 15).

Table 15: Terbutryn concentration [µg/l] in STP effluents

	June 2005	September 2005
STP Eberstadt	0.33	0.25
STP Darmstadt	0.08	0.09
SPP Nauheim	--	0.12
STP Pfungstadt	0.03	0.03
STP Weinheim	2.53	1.72

The mean terbutryn concentration at site We3 was 1.2 µg/l, but was lower elsewhere in the Weschnitz River (Figure 17). Even at sampling site We6, located further downstream close to the mouth of the Rhine River, the terbutryn concentration was still high (0.7 µg/l).

In Modau river a significant increase of the terbutryn concentration occurred between the Mo1 and Mo2 sampling sites (respectively between Mo1 and Sa1; downstream from Mo1 part of river Modau splits into Sandbach, see Figure 2). Spot sampling of the effluent of the Eberstadt and Pfungstadt STPs, located between these sampling sites, revealed a terbutryn concentration not exceeding 0.4 µg/l. The terbutryn concentration in the effluent of the Eberstadt STP was approximately 0.3 µg/l, but only 0.03 µg/l in the effluent of the Pfungstadt STP (Table 15). However, the concentration at the Mo2 sampling site, located downstream from the latter STP, was significantly higher (0.6 µg/l, n = 13). The concentration of terbutryn further down the Modau and Sandbach rivers remained at an almost constant high level between 0.5 µg/l (Mo4) and 0.8 µg/l (Sa1).

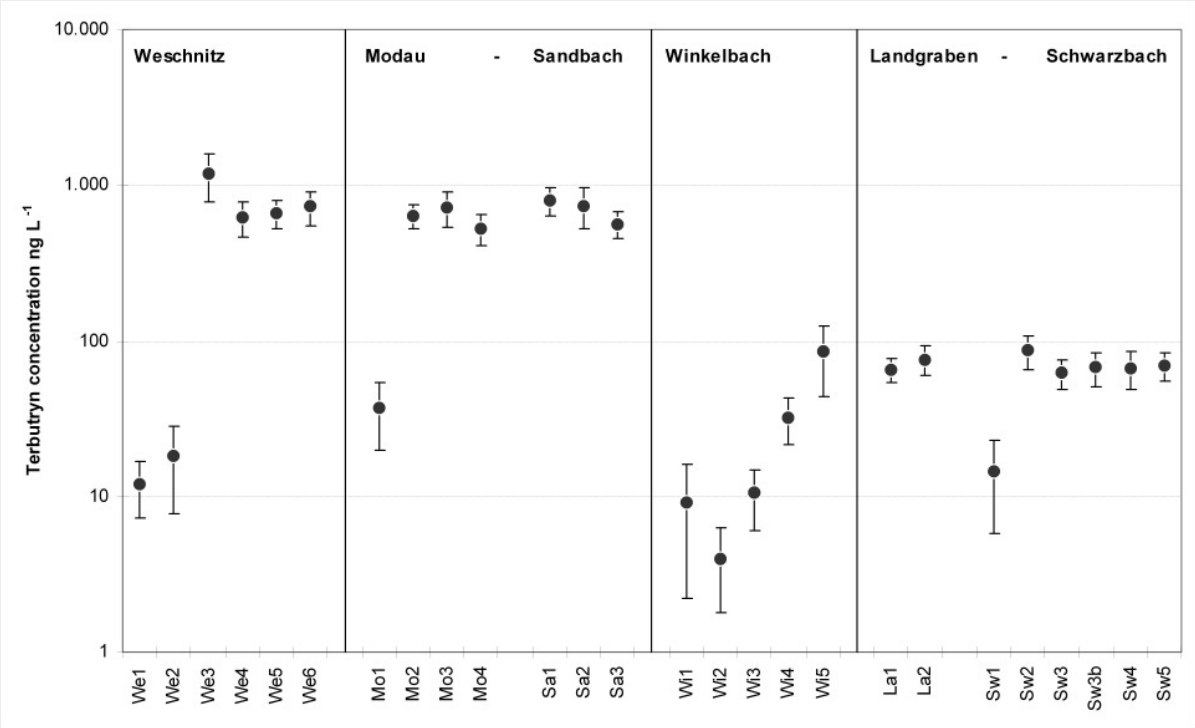


Figure 17: Mean terbutryn concentration and standard deviation at sampling sites

Concentrations of terbutryn in the Schwarzbach–Landgraben river system were much lower than in the Weschnitz and Modau rivers, and remained relatively constant. The mean concentration ranged between 0.06 µg/l and 0.08 µg/l, with the exception of sampling site Sw1, where the concentration was below the detection limit. Moreover, the effluent of the Darmstadt and Nauheim STPs had average terbutryn concentrations of 0.1 µg/l (n = 3), far below that in the effluent of the STPs discharging into the Modau and Weschnitz rivers. Other STPs discharging into the Schwarzbach–Landgraben system have not been sampled, but the low terbutryn concentrations in this river systems suggests they are not major contributors to the terbutryn load of these rivers.

The Winkelbach River had the lowest terbutryn concentration of all river systems in the study. In general, no terbutryn was detected at sampling sites Wi1, Wi2 and Wi3. Downstream, terbutryn (0.04 µg/l) was commonly detected at Wi4 . Between Wi3 and Wi4 the small Lindenbruchgraben Creek discharges into the Winkelbach River (see Figure 2). This creek is a receiving stream for the Bensheim STP, which might be the source of the terbutryn in the downstream sampling sites of Winkelbach River. Further downstream in the Winkelbach River, between Wi4 and Wi5, the Langer Graben Creek discharges into the Winkelbach River, which may explain the increased mean terbutryn concentration (0.08 µg/l) at site Wi5. From all sampling sites on the Winkelbach River, only Wi1 was not influenced by effluent

from STPs. Nevertheless, traces of terbutryn (0.02–0.07 µg/l) were detected at this site on three occasions during the sampling period.

6.4.2 Temporal variations in terbutryn in the Hessisches Ried catchment area

Temporal patterns in terbutryn concentrations were found in the Hessisches Ried river systems. In general, concentrations of terbutryn were higher during summer and autumn than in winter and spring. However, there was high variability among different river systems. For example, the Weschnitz River had the highest mean terbutryn concentration in June 2004 (1.8 µg/l), but the concentration in the Modau River at this time was approximately 0.5 µg/l. In the following sampling period (October 2004) the concentration in the Weschnitz River decreased to 0.8 µg/l, which was still above the overall average for this river system, but the average terbutryn concentration in the Modau River (1.7 µg/l) was the maximum found for this river.

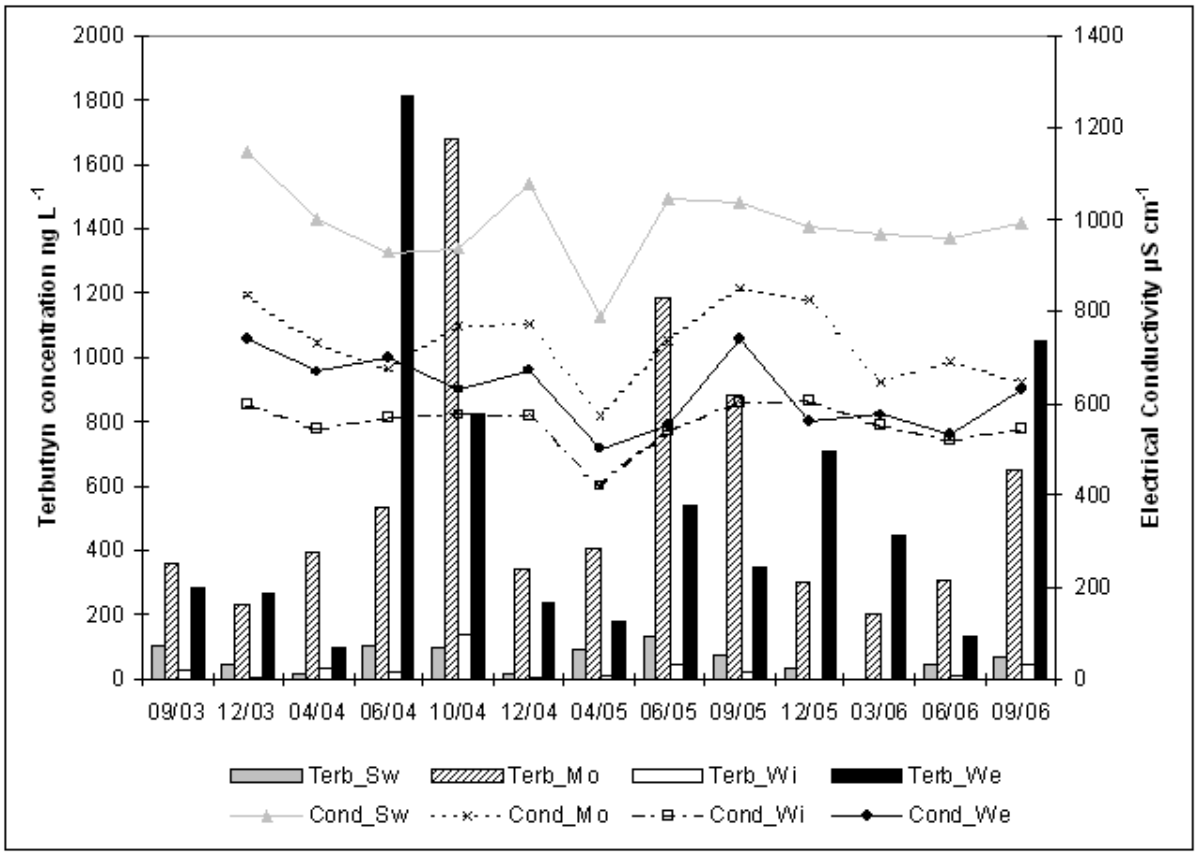


Figure 18: Temporal variation of terbutryn concentration (Terb) and electrical conductivity (Cond) in Schwarzbach River (Sw), Modau River (Mo), Winkelbach River (Wi) and Weschnitz River (We)

The temporal variations in terbutryn concentration can partly be correlated with the discharge rates of the river systems. For example, high water levels associated with the high discharge rates in April 2005 resulted in a decrease in electrical conductivity of the water (584 µS/cm, compared to the mean of 760 µS/cm) and consequently in dilution of the pollutants (Figure 18). However, variability in discharge rates cannot explain all of the observed temporal variations in terbutryn concentrations in the river systems. Figure 19 shows the water discharge loads of terbutryn at representative sites in each of the four river systems, and reveals different trends among rivers. The discharge loads of terbutryn in the Winkelbach and Schwarzbach rivers were similar, with lower loads in winter and spring, and for both rivers the concentrations of terbutryn were negatively correlated with the amount of discharge at sampling sites with comparatively high loads. The input of terbutryn into these systems appears to remain at a constant level, so the decreased concentrations of terbutryn with increasing river discharge indicate that terbutryn in these rivers is simply diluted. Figure 20 illustrates the observed discharge–concentration relationships.

A similar correlation was not evident for the Weschnitz and Modau–Sandbach rivers, and at sampling site Mo2 there was a positive correlation between river discharge and concentration. In all river systems assessed there was no decrease in the overall discharge loads of terbutryn in the period 2003 to 2006.

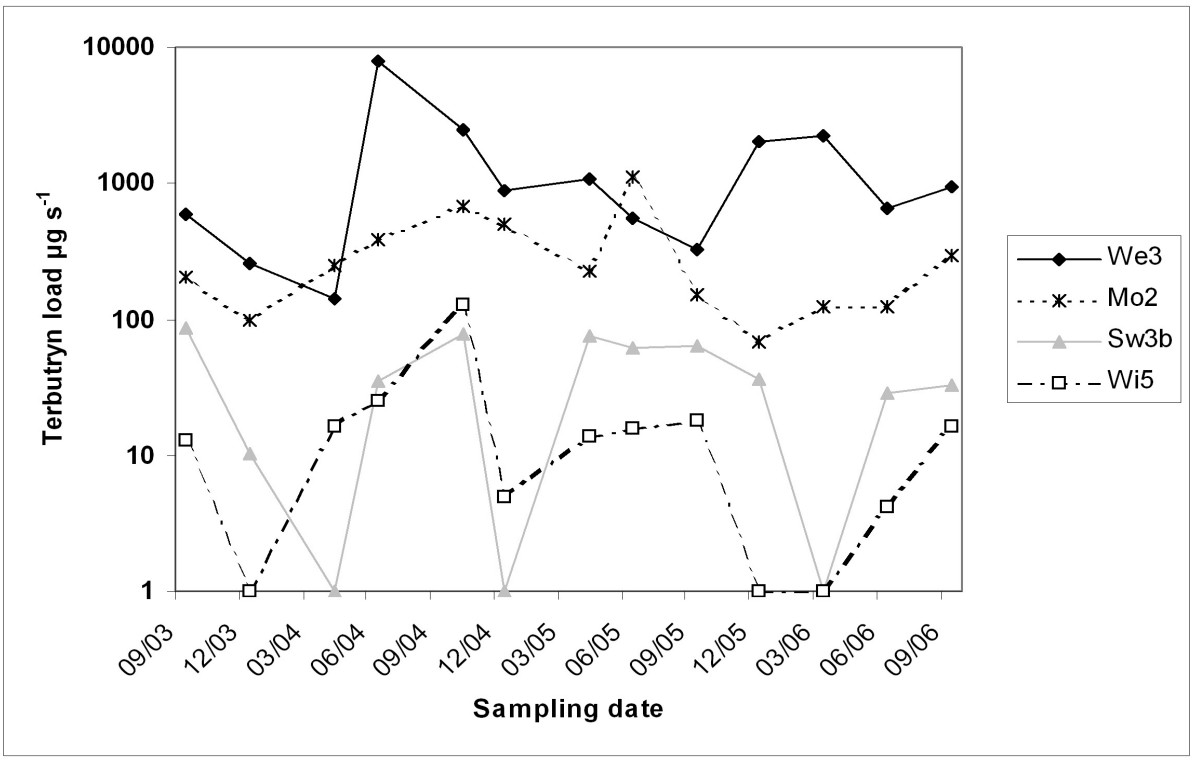


Figure 19: Temporal variation of terbutryn load at four sampling sites

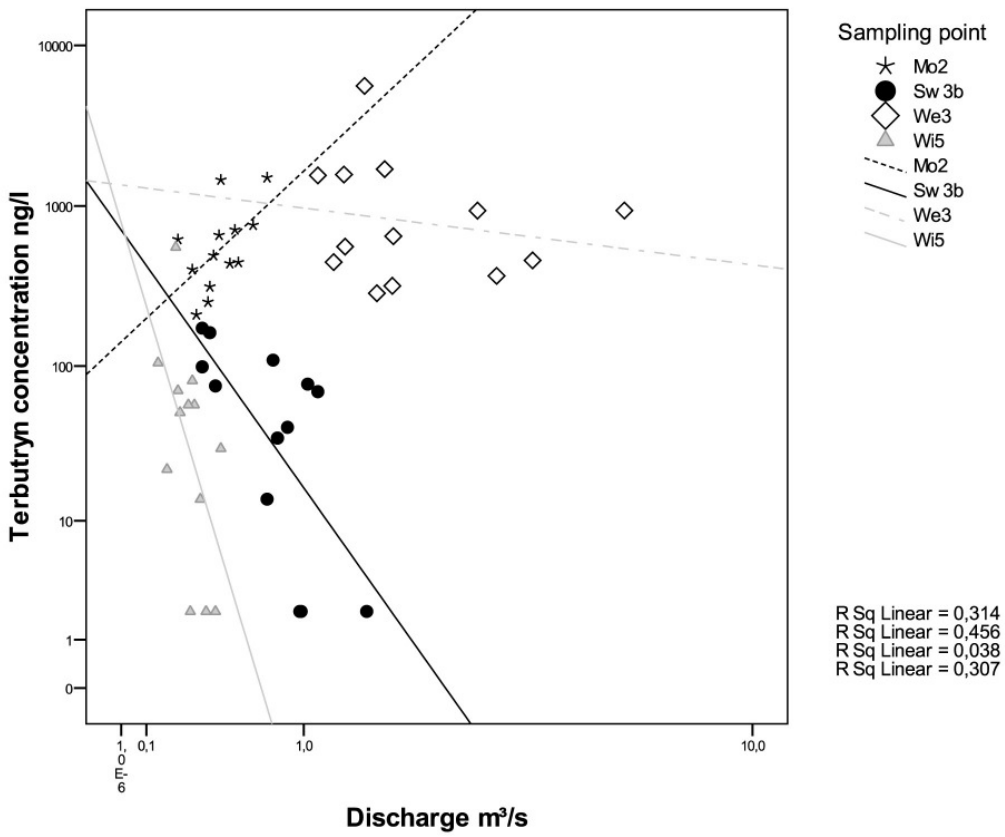


Figure 20: Relationship between terbutryn concentration and discharge at four sampling sites

6.5 Discussion

Observed terbutryn concentrations were high in two (Weschnitz, Modau) of the four analyzed river systems of Hessisches Ried. Comparable concentrations have only previously been reported from STP effluents (Kuch, 2005). Adverse effects of terbutryn on aquatic organisms are likely at this concentration: a decrease in primary production of periphytic algae at a concentration of terbutryn above 0.6 µg/l has been reported in experiments in an artificial water stream system (Brust et al., 2001). A recent study (Bayrisches Landesamt für Umwelt, 2007) on pesticides in Bavarian rivers reported high detection frequencies especially for three triazine components and their degradation products: atrazine, desethylatrazine, terbuthylazin, desethylterbuthylazin and terbutryn. Reported maximum concentrations for atrazine and terbuthylazine (0.1 µg/l and 0.32 µg/l, respectively) were about in the same range as in the present study, but maximum terbutryn concentrations (0.14 µg/l) were far below the level observed in the Weschnitz and the Modau river. This indicates the existence of a regional problem in the catchment areas of these rivers. In contrast, the observed terbutryn

concentrations in Winkelbach and Schwarzbach river were in the lower nanogram per liter range and correspond to the monitoring results of other studies from various German rivers (Bayrisches Landesamt für Umwelt , 2007; LUA-NRW, 2002; UBA, 2004).

The results show that STP effluents are relevant sources for terbutryn found in the rivers but differ largely in the level of discharged terbutryn amounts. In all river systems, with the exception of the Modau – Sandbach system, the terbutryn concentrations found in the STP effluents were in the range of those found in the associated rivers. Especially in case of the Weschnitz river the results suggest that the Weinheim STP was a major source of terbutryn in the Weschnitz River during the sampling period. In contrast, there is no obvious explanation for the relatively high terbutryn concentrations observed in the Modau River. The results indicate that there is an unidentified source of terbutryn discharging into the river which is located somewhere between Mo1 und Mo2 (between Mo1 and Sa1, in the Sandbach River). Furthermore, the results indicate that STP effluents cannot be the only sources of terbutryn in the rivers. This is illustrated by the sampling site Wi1 which is not influenced by STP effluents but even though shows occasionally terbutryn occurrence at low concentrations. Downstream from Wi1 the river is largely diked, which obstructs the direct inflow of surface waters. However, abundant small artificial ditches drain the surrounding agricultural area, and these may discharge into the Winkelbach River.

In situ biodegradation of terbutryn in rivers can be expected to be of minor importance since terbutryn in water is subject to very slow biodegradation (Muir, 1980; Muir and Yarechewski, 1982). Field studies (Muir et al., 1981) have shown that the half life of terbutryn in water of farm ponds varies between 21 and 30 days, which is far above the maximum residence time of 19 h calculated for water flow from site We1 to the river mouth. Photochemical degradation is regarded an important transformation pathway for triazine herbicides (Konstantinou et al., 2001; Lanyi and Dinya, 2003; Lanyi and Dinya, 2005). In laboratory experiments, Kiss et al. (2007) observed decomposition of terbutryn within 32 h, but it would be problematic to assume this high degradation rate also under field conditions.

The analysis of temporal terbutryn patterns revealed that the ban on agricultural use of terbutryn at the end of 2003 had no discernable influence on river loads in the Hessisches Ried region. It may be that terbutryn is still being used in agriculture despite the ban, or terbutryn may be originating from other sources, such as roof paints. Another possibility is redissolution from sediments and soils. Based on a log K_{OW} of 3.7, terbutryn will adsorb to sediment and suspended particulate matter. Half-lives of 240 and 180 days have been reported for degradation of terbutryn in pond and river sediment, respectively (Muir and Yarechewski,

1982), so the existence of a terbutryn pool in the sediments of the sampled river systems is probable. Mobilization of terbutryn will be increasing at increased temperatures that can be found in summer an early autumn since desorption is an endothermic process. Therefore, higher terbutryn concentrations and loads in summer and autumn can also be provoked by sorption processes. Furthermore, minor redissolution from the sediment and/or leaching from groundwater could also explain the observed low terbutryn concentrations in winter, when agricultural use can be largely excluded. Atrazine was still abundant in many aquifers years after it was banned, and leaching from the soil into the groundwater was suggested as a main reason (Barth et al., 2007; Tappe et al., 2002). In addition, s-triazines adsorbed on clay minerals in soil persist over long periods and desorb only gradually (Herwig et al., 2001); a similar process may also occur for terbutryn. Spot sampling of 8 groundwater dwells along the river system in July 2005 revealed terbutryn (0.4 µg/l) in groundwater near sampling site We5, which underscores the presence of additional terbutryn sources within the river environment. This argues for a qualitatively and quantitatively high input of terbutryn (high terbutryn concentrations and high loads) to this river, originating perhaps from STP effluents, as already discussed above. Indeed, analysis of terbutryn loads at sampling sites on the Modau and Weschnitz rivers indicates that the observed terbutryn pollution can be ascribed to higher inputs in summer and autumn, and not only to lower river discharges.

6.6 Conclusions

The concentrations of terbutryn were determined over the period 2003 to 2006 in the Schwarzbach−Landgraben, Modau−Sandbach, Winkelbach and Weschnitz river systems of the Hessisches Ried catchment area. Concentrations varied significantly, with high concentrations occurring in the Modau−Sandbach and Weschnitz systems (0.58 µg/l and 0.54 µg/l, respectively) and low concentrations in the Landgraben−Schwarzbach and Winkelbach systems (0.06 µg/l and 0.03 µg/l, respectively). Terbutryn is still present in these river systems and no trend of decreasing concentrations was observed, despite the 2003 ban on terbutryn use as an agricultural pesticide. In spot sampling, two STPs (Weinheim and Eberstadt) were identified as significantly contributing to the terbutryn found in the Weschnitz and Modau rivers. Terbutryn concentrations were generally higher in summer during the main season of, pesticide use. It is well known that pesticides may enter STPs via the sanitary sewer system, through cleaning of agricultural equipment at the farm (e.g. flushing of pesticide-containing tanks before refilling with another pesticide) (Seel et al.,

1996). Moreover, both STPs are situated near agricultural areas and presumably receive wastewater from farms. However, other STP effluents (Nauheim, Pfungstadt and Darmstadt) had only low terbutryn concentrations, suggesting the importance of wastewater composition entering STPs. However, in absence of detailed pesticide application dates and volumes in the Weschnitz and Modau area, additional sources for terbutryn in the rivers have to be taken into account, such as higher mobilization from the sediment due to higher water temperatures during summer times. Furthermore, sources other than agriculture (i.e. roof- runoff) might explain the occurrence of terbutryn in the rivers during winter, when farm pesticide application typically ceases. Based on its similarities with atrazine, the possibility of redissolution of terbutryn from sediment and leaching from groundwater needs to be considered, and will be the subject of further investigations.

7 Concentration of organic pollutants in the aquatic environment: Influence of mandatory regulations and voluntary environmental agreements

7.1 Abstract

Four common organic pollutants—tris(2-chloroethyl)phosphate (TCEP), the technical isomer mixture of 4-nonylphenol (NP), 2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn) and N,N-diethyl-m-toluamide (DEET)—were monitored in small freshwater streams in the Hessisches Ried region, Germany, during the period September 2003 to September 2006. These substances are subject to differing regulations. Whereas the use of NP and the related nonylphenolethoxylates (NPEOs) is almost completely banned under EU directive 2003/53/EG, the herbicide terbutryn is only restricted for use as a herbicide in the majority of member states of the European Union (EU). In contrast, TCEP and DEET are not regulated by legislation but have been replaced in some products through consumer pressure. For example, Bayrepel has replaced DEET in insect repellents produced by Bayer A.G., and TCEP is nowadays replaced by tris(1-chloro-2-propyl)phosphate (TCPP) as a flame retardant and plasticizer. Monitoring in the study area revealed a significant concentration decrease only for NP, indicating that the strict regulation of NP and NP ethoxylates has led to a significant improvement in reducing the occurrence of this compound in the aquatic environment. For the other three compounds no significant concentration decrease was observed. The impact of regulation on the environmental concentrations of these pollutants is discussed.

7.2 Introduction

In the last decade, studies (Boyd et al., 2003; Daughton and Ternes, 1999; Dsikowitzky et al., 2004a; Kolpin et al., 2002; Poiger et al., 2003) have increasingly targeted the so-called emerging pollutants such as pharmaceuticals, personal care products, surfactants, flame retardants, and industrial and agricultural chemicals. These chemicals are typically characterized by high production volumes, high polarity, low biodegradability and consequent ubiquitous occurrence in the aquatic environment, and are the subject of public and scientific concern due to unknown or possible adverse effects on the environment and human health. As

a result, the legislature of many countries presently endeavors to minimize risks by implementing new laws and regulations. In the European Union (EU), implementation of the Water Framework Directive no. 2000/60/EC of the European Community represents one approach to managing these new emerging pollutants. The directive defines a priority list of 33 substances or groups of substances of major concern for waters, and issues water quality objectives directed at achieving a "good ecological state" for surface waters. Another legal measure is the European Union regulation 2006/1907 of 18 December 2006, which regulates the registration, evaluation, authorization and restriction of chemicals (REACH). However, chemicals have been prohibited in the past with varying success for affected environments. In Germany, for example, the pesticide atrazine was banned in 1991 but was still detected in sewage treatment plant (STP) effluent in 1997 (Nitschke and Schussler, 1998), and was found as a diffuse contaminant in groundwater until recently (Tappe et al., 2002). In France the use of atrazine has been banned since September 2003, but a significant decrease in the concentration of this compound and its metabolite desethylatrazine has not been observed in the groundwater of an agricultural catchment in Breville, France (Baran et al., 2007; Barth et al., 2007). Voluntary agreements by manufacturers to abandon use of some substances has played a major role in the past. For example, removal of phosphate from washing agents in the mid-1980s in Germany lead to a noticeable improvement in surface water quality. However, the effectiveness of voluntary environmental programs and regulation is in question (Anton et al., 2004; Arimura et al., 2007; Blackman, 2007; Jimenez, 2007; Khanna, 2001; Morgenstern and Pizer, 2007). For example, Arimura et al.(2007) found two voluntary environmental actions (the ISO 14001 standard and public environmental reports) to be effective in reducing natural resource use, solid waste generation and water wastage. Others (e.g. Morgenstern and Pizer, 2007) have examined various voluntary environmental programs in the USA, Japan and the EU, and found the effects to be low (0 – 28 %). Moreover, Ziegler and Rennings (2004) investigated the determinants of environmental innovation in firms and found that the European EMAS standard had no significant effect on environmental innovation.

In the present study the occurrence of four common surface water pollutants was investigated in rivers of the Hessisches Ried catchment area near Frankfurt, Germany. These compounds have the characteristics of "emerging pollutants", and include the insect repellent N,N-diethyl-m-toluamide (DEET), the chlorinated flame retardant tris(2-chloroethyl)phosphate (TCEP), the herbicide 2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn), and the technical mixture 4-nonylphenol isomers (NP), which are the degradation products of

synthetic non-ionic surfactants (4-nonylphenol ethoxylates). The four compounds have different regulatory statuses. Under European Directive 2003/53/EG the use of NP and the related ethoxylate has been strictly prohibited in the EU since January 2005. Prior to this, NP use was subject to a risk assessment designed to yield predicted-no-effect concentrations (PNEC) of only 0.33 µg/l in the aquatic environment. NP can disrupt the endocrine system by interfering with the estrogen receptor (Jobling and Sumpter, 1993). Apart from endocrine disruption, NP causes long-term toxic effects on aquatic organisms at concentrations of 3.3 µg/l (ECB, 2002). From the 1980s to the early 2000s, NP was often detected in surface and wastewaters (reviewed by Thiele et al., 1997). Concentrations of NP in rivers in the 1980s occasionally reached values above 10 µg/l (Ahel et al., 1994a; Schaffner et al., 1987). Since the endocrine disruption and toxicity of NP was evident (McLeese et al., 1980; Soto et al., 1991), the alkylphenolethoxylate-manufacturing industries in Germany decided in 1986 to voluntarily replace alkylphenolethoxylates (APEOs) in household, and later industrial, detergents. A significant decrease in NP concentration in sewage sludge (Jobst, 1998) and surface waters (Leisewitz and Schwarz, 1997) has been recorded since that time. However, despite this decrease the concentration of NP remained at high levels in STP effluents and in receiving waters (Bolz et al., 2001) in Germany in the late 1990s (Hegemann et al., 2002). NP concentrations up to 1.2 µg/l were still being reported in rivers in Germany in the early 2000s (Fries and Püttmann, 2003b).

The herbicide terbutryn is regulated by the European Council Directive 91/414/EEC and the European Commission Regulation (EC) 2076/2002. Under these regulations authorization of plant protection products containing terbutryn was withdrawn on 25 July 2003 (with a period of grace that expired on 31 December of 2003) for all members of the EU with the exception of the UK, Spain, Ireland and Slovakia, where authorization is due to expire not later than 31 December 2007. In contrast, DEET and TCEP are not yet regulated by legislation but have been voluntarily replaced by the main producers as a result of public concern. The risk of serious medical effects of DEET appears to be low (Bell et al., 2002) when applied with common sense, but in rare cases it has been toxic to humans (Davies et al., 1988; Koren et al., 2003; Roland et al., 1985). DEET is rapidly absorbed through the skin, metabolized and eliminated in the urine (Selim et al., 1995). It has also been suggested to be involved in Gulf War Syndrome, causing toxic side-effects due to synergistic interaction with other neurotoxic substances (Haley and Kurt, 1997). In 1999 the Bayer group substituted the active agent in their products. For example, in the insect repellent Autan®, DEET was replaced by Bayrepel (1-piperidinecarboxylic acid, 2-(2-hydroxyethyl), 1-methylpropyl ester), which is as efficient

as DEET and has no known adverse effects (Wahle et al., 1999a; Wahle et al., 1999b). However, there are still products on the market containing DEET as the active agent. In Greece DEET is used for indoor control of insects through vaporization of DEET-containing tablets in wall-mounted electric heating elements that slowly release the insecticide (Dall'Osto et al., 2007). In a recent review of the worldwide occurrence of DEET in the aquatic environment, concentrations ranging from 40–3000 ng/l in various water bodies (Costanzo et al., 2007) were reported. In Germany DEET was found in surface waters at concentrations of up to 90 ng/l in Lippe (Dsikowitzky, 2002), 80 ng/l in the Rhine River (Knepper et al., 1996), and at 1.1 ng/l in maritime waters of the North Sea (Weigel et al., 2002).

TCEP is a flame retardant and plasticizer. The estimated consumption of TCEP in Germany in 1997 was 500–1000 t (Leisewitz et al., 2001a), and on a global scale was about 4000 t per annum in 1998 (ECB, 2006). Until the mid-1990s TCEP was used in a mixture of about 1:1 (Leisewitz et al., 2001b) with tris(1-chloro-2-propyl)phosphate (TCPP) as a flame retardant in polyurethane foams. As flame retardants evaporate from consumer products (Kemmlein et al., 2003) TCEP was detected in indoor air (Hartmann et al., 2004; Ingerowski et al., 2001) and house dust (Marklund et al., 2003). TCEP has been shown to be carcinogenic and neurotoxic to animals (Tilson et al., 1990; Umezu et al., 1998), and in the early 1990s the European Isocyanate Producers Association (ISOPA) recommended replacement of TCEP. The two German producers have ceased TCEP production, and it is replaced by TCPP in polyurethane foams (Fooken, 1997). According to the European Flame Retardants Association (EFRA), TCEP is no longer produced in the EU-15 member states (Leisewitz, 2006), but processing/use of TCEP is not prohibited. Imports of TCEP to the EU in 2001 amounted to about 1150 t (ECB, 2006). TCEP is on the second EU priority list and currently a risk assessment is carried out. The risk assessment draft of 2 March 2006 proposed a PNEC for water of 65 µg/l (ECB, 2006). As TCEP is commonly present in wastewater and is not eliminated in STPs (Fahlenkamp et al., 2004b; Höhne and Püttmann, 2006b; Meyer and Bester, 2004), it enters the aquatic environment via this route (Fries and Püttmann, 2003a; Prösch et al., 2002). Consequently, TCEP is often found in STP effluents and receiving rivers (Andresen et al., 2004; Fries and Püttmann, 2003a; Metzger and Möhle, 2001; Prösch et al., 2000).

7.3 Methods and Materials

7.3.1 Study area and sampling

The study area is in the Hessisches Ried region, south of Frankfurt am Main, Germany. This is a densely populated and industrialized area which also supports agriculture. It is drained by four small rivers (the Schwarzbach, Modau, Winkelbach and Weschnitz rivers), all of which are tributaries of the Rhine River and serve as receiving waters for treated wastewater. Figure 2 provides an overview of the study area and the location of sampling sites. These river systems discharge only small water volumes on an annual basis (Göbel, 1996): 0.3 m³/s for the Winkelbach River, 1.1 m³/s for the Modau, 2.0 m³/s for the Schwarzbach, and 3.2 m³/s for the Weschnitz. The Schwarzbach and Weschnitz rivers receive the greatest volumes of treated wastewater, but due to the larger volume of the latter the proportion of wastewater in the flow at its mouth is lowest (15 %). In contrast, the Winkelbach, Modau and Schwarzbach rivers contain a high proportion of wastewater (47 %, 35 % and 50 %, respectively) at their mouths. In extremely dry seasons the discharge of the Schwarzbach River can comprise almost 100 % wastewater.

A total of 330 water samples were collected during 13 sampling occasions from 26 sampling sites between September 2003 and September 2006. Parameters including water temperature, conductivity and pH were recorded at each site during sampling. A volume of 2.5 l of surface water was collected at each of the 26 sampling sites, stored in a brown glass bottle and kept cool (4°C) during transport to the laboratory. Samples were processed the day after sampling.

7.3.2 Sample preparation and analysis

Samples were passed through pre-cleaned paper filters (Schleicher & Schuell, grade 597½) and then extracted by passage at low pressure (approximately 800 mbar) through solid phase extraction (SPE) cartridges (Bond Elut, 1 ml). Prior to use the cartridges were rinsed with 1 ml methanol and then conditioned with 1 ml methanol/acetonitrile (50:50) and 1 ml distilled water. The SPE cartridges were eluted three times with 333 µl of a methanol/acetonitrile mixture (50:50). The solvent was removed under a nitrogen stream and the extract residue was dissolved in 100 µl acetonitrile. Squalane (4000 ng) was added to each extract as an internal standard. The extracts were subjected to GC-MS analysis using a Fisons GC 800 gas chromatograph equipped with a BP-X5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness), and with helium as the carrier gas. The GC oven temperature varied from 80°C to 300°C at a rate of 4°C per minute. Extracts (1 µl) were

injected in splitless mode. The mass spectrometer (Fisons MD 800) used electron ionization (EI, 70 eV) and was operated in full-scan mode (50–600 m/z). The analytes were identified by comparison with reference standards of terbutryn, 4-nonylphenol, 4-n-nonylphenol and DEET (Ehrenstorfer), and TCEP (Sigma Aldrich).

Table 16: Analytical parameters of target compounds.

	Quantifier ion	Qualifier ions	LOD ng/l	LOQ ng/l	Recovery %
Terbutryn	226	185, 170, 241	4	13	80
DEET	119	91, 190	8	23	81
TCEP	63	205, 207, 249, 251	5	14	110
4nNP	107	220	8	25	77
4NP					
isomer group I	149	121, 107, 191			
isomer group II	135	107, 121			
isomer group III	121	163, 177, 149			
isomer group IV	177	121, 177, 149, 163			

Table 16 provides information on the mass traces used for the extract components. The method of Fries and Püttmann(Fries and Püttmann, 2003b) was used for quantification of the 4-nonylphenol isomers. Detection and quantification limits were determined in accordance with DIN 32 645(1994), and ranged between 4 ng/l and 8 ng/l and 13 ng/l (Table 16), respectively. For calibration, standard solutions of TCEP, NP, terbutryn and DEET were prepared at 2, 1, 0.2, 0.1, 0.05, 0.02, 0.005, 0.002 and 0.001 µg/l. Recoveries were between 77 % and 110 %.

7.4 Results and discussion

7.4.1 NP (technical isomer mixture)

For the NP technical isomer mixture a maximum concentration of 0.77 µg/l was detected in the Schwarzbach River in September 2003, when overall highest concentrations (compared to the other sampling periods) were detected. After September 2003, the mean NP concentrations decreased from 0.4 µg/l to 0.02 µg/l (in September 2006), and the detection frequency of NP in the water samples decreased. Whereas in September 2003 NP was present in all samples at concentrations above the detection limit of 0.008 µg/l, in September 2006 NP could be detected in only 60 % of the samples. During two sampling campaigns, in April 2005 and June 2005, NP was not detected in any water sample analyzed. In total, NP was

detected in 56% of the water samples. In addition to decreased concentrations, mean NP loads decreased from 256 µg/s in September 2003 to 9 µg/s in September 2006 (Figure 21). The decreasing loads indicate that the observed NP decrease was due to lower inputs, and not just a function of dilution effects due to higher discharge volumes. The decrease in NP can be attributed to implementation of European Directive 2003/53/EG, which has prohibited the use of NP and related nonylphenolethoxylates (NPEOs) in industrial and commercial cleaning agents since January 2005. Similar outcomes have also been observed in wastewaters and rivers in Switzerland(Voutsa et al., 2006), and from STP effluents in Germany (Höhne and Püttmann, 2006a). Moreover, in a previous study (Quednow and Püttmann, 2008) we investigated the occurrence of octylphenol (OP) in river water, and found that in contrast to NP, the concentration of OP showed no decrease in the Hessisches Ried rivers during the same sampling period. OP and the related octylphenolethoxylates (OPEOs) have similar applications to NP, but have not yet been banned. Despite these results, at the end of the sampling campaign in September 2006 NP was still present in the study rivers, albeit only in small concentrations (average approximately 20 ng/l). Although the EU directive bans the use of NP and NPEOs in textiles within the EU, there is no ban on imported textiles containing these substances. In a recent study for the Swedish Society for Nature Conservation (SSFNC) (Hök, 2007), the NPEO content of 20 towels produced by different companies was analyzed, and NPEOs were found to be present in all samples at concentrations up to 10.6 g/kg. On the basis of these results the SSFNC estimated the amount of NP imported in textiles from countries outside the EU and entering STPs was 9 t/a in Stockholm alone. Furthermore, a representative from SASOL Germany, a producer of APEOs, estimated the quantity of NPEOs in textiles imported to the EU to be 500–1000 t/a (C.D. Hager, pers. communication, 2006). Therefore, imported textiles still represent an important source of NP entering the aquatic environment in Europe. Apart from imported products, plant protection substances can also be a source of NP entering aquatic environments, since NP is still used as an emulsifying agent in some pesticides (Guenther et al., 2002). The use of these products was not prohibited with implementation of European Directive 2003/53/EG. In addition, diffuse sources including re-solution from river sediments has to be considered, since NP tends to adsorb to suspended matter and is often found in sediments (Bolz et al., 2001; Croce et al., 2003; Fu et al., 2007; Heemken et al., 2001; Isobe et al., 2001; Li et al., 2004). Although data on NP in sediments of the study rivers are not available, it is likely that sediments represent an NP pool as a result of high NP fluxes in the past.

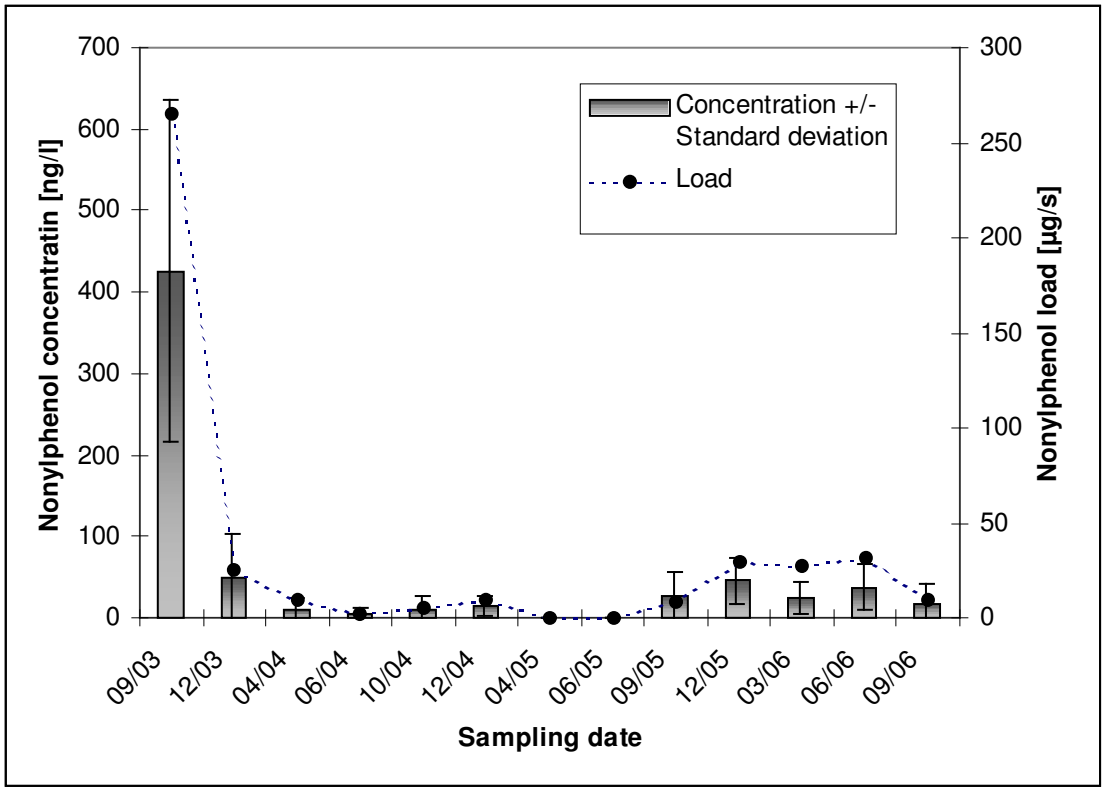


Figure 21: Nonylphenol concentration and load from September 2003 to September 2006 in rivers of the Hessisches Ried region.

7.4.2 TCEP

Mean TCEP concentrations in the study rivers varied significantly, from 328 ng/l in the Schwarzbach River to 242 ng/l in the Modau River, 108 ng/l in Weschnitz River, and 71 ng/l in the Winkelbach River (Table 17).

Generally, TCEP concentrations were higher at sampling locations that were influenced by high wastewater input, including all sampling locations of the Schwarzbach–Landgraben River with the exception of Sw1, and all sampling locations near the mouths of the Weschnitz, Modau and Winkelbach rivers. Furthermore, a positive correlation (R = 0.5) between TCEP concentration and associated population equivalent was observed. The highest TCEP concentrations (up to 2 µg/l) were found in September 2005 in the Schwarzbach River which, together with the Weschnitz River, had the highest transported TCEP loads (201 µg/s and 180 µg/s, respectively). Thus, the input of TCEP into both rivers is roughly the same, with the lower concentrations in the Weschnitz River resulting from dilution due to its greater discharge volume.

Table 17: Concentration and load of target compounds.

Analyt	River		Concentration [ng/l]			Load [µg/s]
DEET		%>LOD	min	max	mean	mean
	Schwarzbach	87	< LOD	1292	245	143
	Modau	72	< LOD	936	82	30
	Winkelbach	46	< LOD	564	70	20
	Weschnitz	69	< LOD	380	64	119
	total	70	< LOD	1292	124	83
TCEP						
	Schwarzbach	99	< LOD	2019	328	201
	Modau	95	< LOD	1190	242	75
	Winkelbach	71	< LOD	561	71	20
	Weschnitz	97	< LOD	464	108	180
	total	92	< LOD	2019	203	127
Terbutryn						
	Schwarzbach	78	< LOD	246	63	42
	Modau	90	< LOD	3067	583	184
	Winkelbach	40	< LOD	554	28	7
	Weschnitz	75	< LOD	5600	536	976
	total	73	< LOD	5600	306	292
NP						
	Schwarzbach	53	< LOD	770	44	29
	Modau	60	< LOD	723	62	19
	Winkelbach	55	< LOD	618	48	13
	Weschnitz	56	< LOD	717	40	62
	total	56	< LOD	770	49	31

The lowest TCEP concentration and load (average 71 ng/l and 20 µg/s, respectively) were in the Winkelbach River, which can be attributed to the low wastewater input and generally low discharge volumes (Table 17) in this river. TCEP loads in the Modau River were intermediate (75 µg/s) because only small STP effluent volumes are discharged into the river's lower reaches, and the river has a lower discharge volume relative to the Weschnitz River. Consequently, TCEP concentrations were higher in the Modau River than in the Weschnitz River.

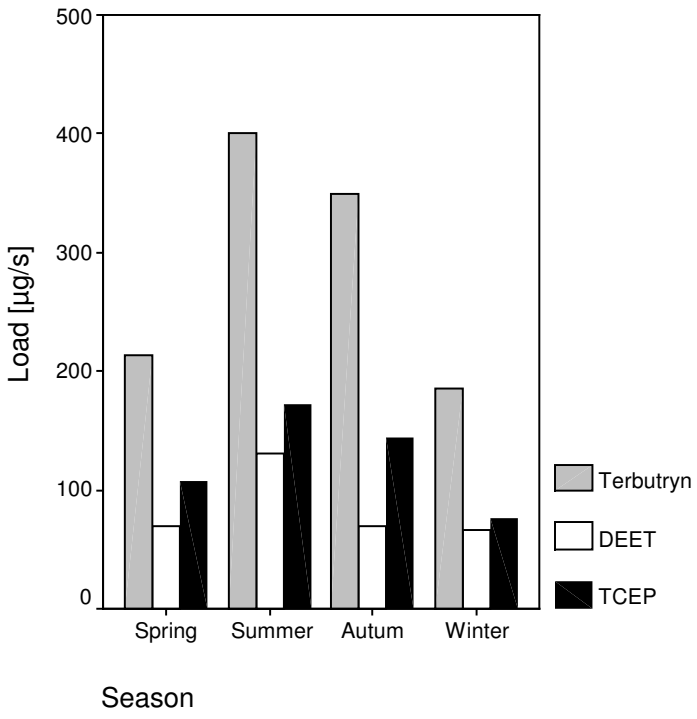


Figure 22: Seasonal variation in mean load of TCEP, DEET and terbutryn in rivers of the Hessisches Ried region

There was temporal variation in TCEP loads, which were significantly higher in summer (173 µg/s) and autumn (146 µg/s) (Figure 22). This was probably due to lower rainwater input and therefore comparatively higher proportions of wastewater being present during these periods. No overall trend of decreasing TCEP concentrations was observed during the study sampling period Figure 23). The detection frequency was about 92 % with a detection limit of 5 ng/l, suggesting that TCEP still present as a flame retardant in consumer products is entering surface waters via STP effluents. This confirms other studies reporting frequent detection of TCEP in various water matrices. Andresen et al.(2004) in 2002 reported STP effluent and river water concentrations of 120 ng/l and 50 ng/l, respectively, in the Ruhr/Rhine area, and Dsikowitzky et al.(2004b) found TCEP concentrations up to 0.2 µg/l in the Lippe River. Prösch et al.(2002) reported decreasing concentrations of TCEP in the 1990s, when most conversion from TCEP to TCPP occurred. However, this measure was clearly not sufficient, with TCEP continuing to enter the aquatic environment via STPs as a consequence of ongoing importation of TCEP-containing products from non - EU states.

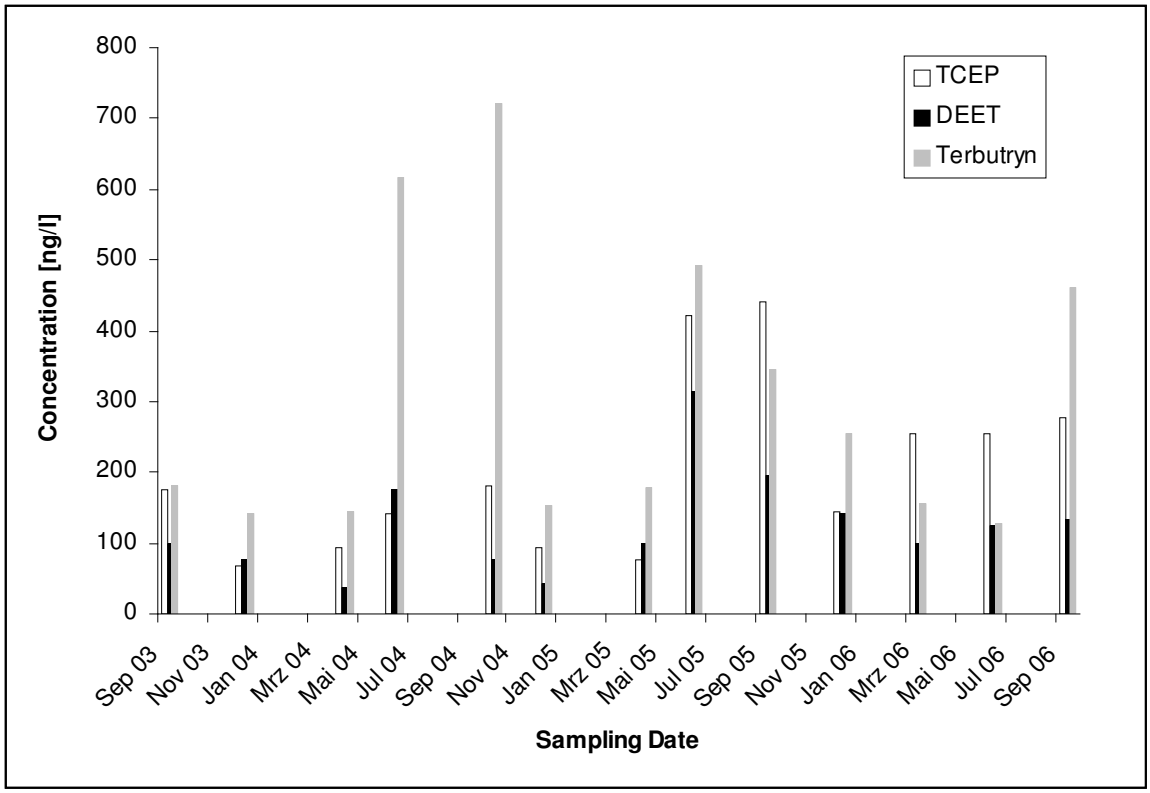


Figure 23: Concentrations of TCEP, DEET and terbutryn from September 2003 to September 2006 in rivers of Hessisches Ried region

TCEP concentrations had previously (1992–2000) been determined in rivers from the same catchment area examined in our study (Fooken, 2000), and a comparison of both data sets is shown in Figure 24. The results show a decrease in the concentration of TCEP in river water around the year 2000, but a further decrease since that time is not evident.

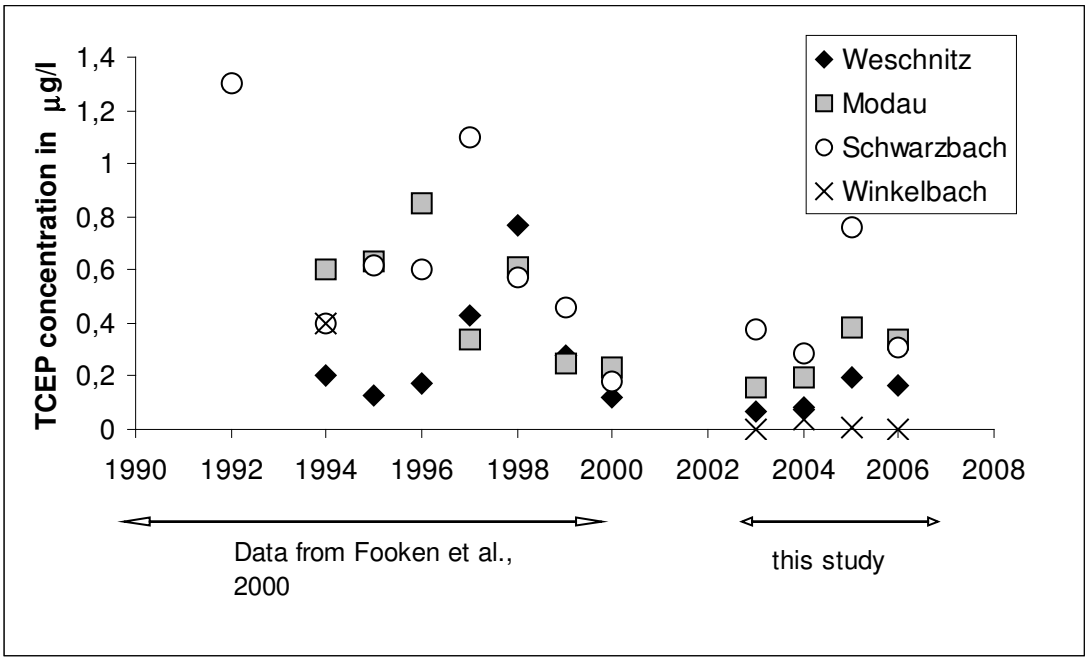


Figure 24: Comparative TCEP concentrations from this and an earlier study

7.4.3 Terbutryn

The occurrence of terbutryn in the study area is shown in Figure 23. The highest terbutryn concentration (5.6 µg/l) was found in June 2004 in the Weschnitz River (We3). This concentration is very high considering that terbutryn is toxic to algae (EbC50 – 72 h) at concentrations of 2 µg/l (Okamura et al., 2000), and has adverse effects on primary production of periphytic algae at concentrations above 0.6 µg/l(Brust et al., 2001). Furthermore, Richter and Nagel (Richter and Nagel, 2007) recently identified water as the primary route of terbutryn uptake in two benthic organisms (*Gammarus fossarum* and *Asellus aquaticus*). They determined bioaccumulation factors of 13 and 30, respectively, in these organisms, indicating a moderate potential for bioaccumulation. Terbutryn concentrations showed a clear spatial trend, with high concentrations in the Weschnitz and Modau rivers (0.54 µg/l and 0.58 µg/l, respectively), and low concentrations in the Winkelbach and Schwarzbach rivers (0.06 µg/l and 0.03 µg/l, respectively). The Weschnitz River had a higher load (399 µg/s) than the Modau River (124 µg/s), indicating greater input of terbutryn. Furthermore, terbutryn loads showed significant peaks in summer and autumn (Figure 22), when application of terbutryn and cleaning of pesticide tanks occurs. These seasonality and strong spatial patterns suggest an agricultural source. Other terbutryn sources, such as roof paints (Menge, 2005), appear to be an unlikely explanation for the high terbutryn load in the Modau and Weschnitz rivers, although terbutryn from roof paints may explain the low terbutryn concentrations found in the upper reaches of the Schwarzbach River, were agricultural use can largely be excluded.

Although application of terbutryn as a herbicide in Germany has been strictly prohibited since 31 December 2003, a trend of decreasing terbutryn concentration in the study rivers was not detected (Figure 23). In contrast to the expected decrease after the ban, terbutryn concentrations were highest in the 2004 growing season. A possible explanation is the deliberate exhaustion of remaining herbicide stocks by farmers. This explanation, however, would not explain the fact that terbutryn levels in the water samples remained at the same levels in 2005 and 2006. Ignoring sources other than agriculture, this suggests that farmers may be obtaining illegal pesticides. A recent Greenpeace study that revealed it is relatively easy to buy illegal pesticides abroad and in Germany included 38 pesticide products containing 11 illegal agents amongst which were bifethrin and diethion, whose application has at no time been permitted in Germany (Greenpeace, 2006). In 2005 a study of pesticides in vegetables revealed that 24 % of samples had residues of illegal pesticides (Greenpeace, 2005). Furthermore, in some European countries including the UK, Spain, Ireland and

Slovakia, application of terbutryn is permitted until the end of 2007, and therefore terbutryn-containing products can be purchased from authorized dealers in these countries.

7.4.4 DEET

The DEET concentrations in river samples are listed in Table 17. Significantly higher mean concentrations (245 ng/l) were found in the Schwarzbach River compared to the Weschnitz, Winkelbach and Modau rivers (64 ng/l, 70 ng/l and 82 ng/l, respectively). The highest overall DEET concentration (1.3 µg/l) was found in the Schwarzbach River in June 2004. High DEET loads were detected in the Schwarzbach and Weschnitz rivers. As for TCEP, the higher discharge of the Weschnitz River results in lower concentrations than, but comparable loads to, the Schwarzbach River. The correlation of DEET concentrations with the population equivalent was also positive (R = 0.5), and the correlation with TCEP was strong (R = 0.62, two-tailed, 0.05 probability level). This is not surprising since both DEET and TCEP are common wastewater ingredients (Dsikowitzky et al., 2004a). In parallel with insect populations, mean DEET concentrations and loads (Figure 22) were significantly higher in summer (0.15 µg/l) than in autumn, winter and spring (0.06 µg/l, 0.04 µg/l and 0.05 µg/l, respectively). In the 1990s, Knepper et al.(1996) found concentration peaks of DEET (0.03–0.08 µg/l) in the Rhine River during summer and autumn, paralleling seasonal application as an insect repellent. In results similar to ours, Knepper et al. detected DEET in the rivers outside the insect season, and later investigations revealed elimination of DEET in STPs only at influent concentrations above 0.3 µg/l, with an elimination rate of about 40% (Knepper and Maes, 2003). Higher influent concentrations only occurred in summer. Furthermore, the occurrence of DEET in sewage water in winter and spring (when DEET application as an insect repellent in Germany is virtually non-existent) may be the result of washing of clothes following holidays in warmer regions (Knepper, 2004a). This explanation seems plausible since DEET is one of the most efficient insect repellents (Fradin and Day, 2002) and is often recommended for travel in the tropics. According to Knepper (2004b), concentrations of DEET in sewage and surface water decreased after 1999 when DEET was replaced by Bayrepel in many commercial insect repellents. However, during our sampling period (September 2003 to September 2006), no trend of further decrease was observed (Figure 23). DEET concentrations varied remarkably over the sampling period and remained at a median level of about 0.06 µg/l, which is in the range of concentrations reported by Knepper in the late 1990s.

7.5 Conclusions

All target compounds were consistently detected in rivers in the study area. The lowest concentration, load and detection frequency over the sampling period were observed for NP, which is subject to the strongest regulation through an EU-wide ban. With respect to NP concentrations in the aquatic environment in the last two decades, we conclude that self-regulation by manufacturers has lead to an improvement in the pollution status of this compound in Germany, but environmental concentrations have not been reduced to an acceptable level (i.e. below the PNEC). In contrast, the 2005 European-wide ban seemed to be effective in preventing the substance from entering the aquatic environment on a large scale.

Concentrations of TCEP, DEET and terbutryn showed no decrease during the sampling period. This is particularly surprising for terbutryn, as it indicates that the 2003 ban on the use of terbutryn as a herbicide has had no detectable effect on the concentrations of this compound in the investigated river systems. TCEP and DEET were both withdrawn before 2000 under voluntary agreements, and concentrations were stable at the 2000 level. Therefore, it appears that neither the ban (terbutryn) nor voluntary withdrawal (TCEP and DEET) at the national level are sufficient to prevent the substances from entering the aquatic environment while they can be readily obtained from abroad. As postulated by Morgenstern and Pizer (2007), it seems that although voluntary programs can offer environmental gains, the benefits of such programs are limited.

8 Final conclusions and future implications

All target compounds were detected more or less frequently within the fresh water streams of the study area. In particular, the organophosphates, the synthetic musk fragrances, and the insect repellent DEET showed an ubiquitous occurrence in the water samples of the Hessisches Ried. Furthermore, during the sampling period, the concentrations of the endocrine disruptors NP, BPA, and OP exceeded more than once the PNEC value so that adverse effects on aquatic organisms cannot be excluded. Although the amount of target compounds was limited in advance, the results of the study (i.e. high concentration and high detection frequency of the target compounds) indicate that there is a constant impact on the water quality and aquatic organisms by xenobiotics and that the input amount exceeds the elimination capacity within these small river systems. Considering that the effect on water organisms is so far only known for a few substances and/or substance mixes, the overall consequences for the aquatic environment can only be assumed. On the contrary, the consequences for water supply works are quite evident. Particularly drinking water treatment plants that use surface water or bank filtration seem to be exposed to an increasing amount of persistent chemicals in their raw water. In the past, some xenobiotics such as pharmaceutics and x-ray contrast media already have been found in drinking and raw water (Baus, 2002, Seitz et al., 2006, Ternes et al., 1998). In the future, water treatment facilities works might be forced to eliminate numerous xenobiotics from the raw water by ever more advanced and expensive technologies, perhaps without significantly improving the water quality compared to the current time.

The spatial and temporal variability of the determined concentrations of the target compounds within the river systems was generally high. Besides the natural discharge variation, obviously discontinuous and diffuse inputs contribute to this variability. Nevertheless, some spatial and temporal trends were observed. For example, usually the highest concentrations were observed in the Schwarzbach system, characterized by the highest proportion of waste water compared to the other river systems. Furthermore, the concentrations of the target compounds were generally higher directly downstream of STP effluents, indicating the STPs as an important pathway for xenobiotics to enter the aquatic environment. In fact, the investigation results identify the STP effluents as the dominating source for the chlorinated organophosphates, the synthetic musk fragrances, and the insect repellent DEET in the rivers of the study area. In this context, to improve the elimination capacity of STPs, the

implementation of an obligatory advanced tertiary treatment phase in STPs is currently discussed, even if this disagrees with the causative principle (BGW, 2005).

Furthermore, the study results also indicate that diffuse sources can cause locally high concentrations of the compounds in stream areas not influenced by STPs, such as in the case of TBP, Terbutryn, or NP. The estimation of diffuse sources such as leaching out of the sediment and field or street runoff were not subject to this study, but represent an important issue for future investigations. For instance, the study results have shown that NP is no longer detected within the STP effluents of the study area since the implementation of the European Directive 2003/53/EG at the beginning of 2005 and congruously NP concentration in the receiving waters has been significantly reduced. However, NP was still detected in the lower nanogram per liter range until the end of the sampling period in September 2006. Therefore, the withdrawal of a chemical does not necessarily result in a complete disappearance within the aquatic environment. Similarly, in the case of the herbicid terbutryn, no decrease of concentrations in the river waters of Weschnitz and Modau was observed, although the application as a herbicide in plant production products was prohibited since 2004. Here, the universal application of the compound as a biocide in roof paints, which is not prohibited, might be an explanation for the continuous occurrence of terbutryn in the river waters. Furthermore, the study results indicate that the benefits of national bans or self-regulations by manufacturers on several chemicals are limited. In contrast, the European-wide ban (of NP) seemed to be effective in preventing the substance from entering the aquatic environment on a large scale and reduced the NP concentration to an acceptable level (i.e. below the PNEC).

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Contents of figures and tables

Figures

Tables

Abbrevations

AHTN	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene
APEO	Alkylphenolethoxylate
BPA	Bisphenol A
DEET	N,N-Diethyl-m-toluamide
GC – MS	Gas chromatography – Mass spectrometry
HHCB	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexa-methylcyclopenta-[γ]-2-benzopyran
INTAFERE	Integrated Analysis of Mobile Organic Foreign Substances in Rivers
K	Correction factor
K_{ow}	Octanol – Water Partitition Coefficient
LAWA	German working group on water issues
LOD	Limit of Detection
LOQ	Limit of Quantification
NP	Nonylphenol (technical mixture)
NPEO	Nonylphenolethoxylate
OP	4.-tert.-Octylphenol
OPEO	Octylphenolethoxylate
PNEC	Predictet No-Effect Concentration
R	Response factor
RC	Recovery rate
SPE	Solid Phase Extraction
STP	Sewage Treatment Plant
TBP	Tri-n-butyl phosphate
TBEP	Tris(2-butoxyethyl)phosphate
TCEP	Tris(2-chloroethyl)phosphate
TCPP	Tris(1-chloro-2-propyl)phosphate
TDCPP	Tris(1,3-dichloro-2-propyl)phosphate
TVO	German Drinking Water Ordinance

Publications

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Appendix

Table 18: Discharge at sample points

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s	m³/s
La1	1.07	0.47	0.41	0.64	1.48	2.19	0.8	0.32	0.19	0.28	0.36	0.26	0.25
La2	0.7	.	.	0.54	0.83	0.87	0.43	0.28	0.26	0.54	0.44	0.43	0.56
Mo1	0.41	0.32	0.40	0.28	0.93	0.77	1.01	0.24	0.15	0.25	0.35	0.23	0.17
Mo2	0.42	0.39	0.56	0.54	0.46	0.65	0.51	0.74	0.24	0.33	0.40	0.31	0.45
Mo3	0.44	0.20	0.48	0.31	0.18	0.22	0.51	0.51	0.12	0.35	0.38	0.29	0.45
Mo4	0.51	0.47	0.69	0.45	0.48	0.51	0.45	0.36	0.32	0.63	0.40	0.40	0.53
Sa1	0.34	0.42	0.31	0.36	0.34	0.34	0.34	0.19	0.15	0.09	0.24	0.20	0.09
Sa2	0.25	0.17	0.17	0.21	0.23	0.18	0.25	0.19	0.13	0.07	0.19	0.12	0.07
Sa3	0.19	0.22	0.25	0.20	0.10	0.30	0.31	0.17	0.12	0.11	0.17	0.15	0.08
Sw1	0.31	0.03	0.13	0.10	0.13	0.53	0.19	0.04	0.01	0.06	0.20	0.06	0.01
Sw2	0.61	0.40	0.57	0.49	0.70	1.09	0.72	0.23	0.18	0.37	0.61	0.39	0.30
Sw3	0.86	0.92	1.46	0.90	1.03	1.12	1.26	0.60	0.51	1.27	1.26	0.96	0.98
Sw3b	0.78	0.74	0.98	0.36	0.61	1.54	1.11	0.36	0.40	0.88	0.97	0.81	0.43
Sw4	0.69	0.52	0.81	0.43	0.70	1.00	0.83	0.38	0.21	0.41	0.86	0.61	0.46
Sw5	0.62	0.95	1.25	1.05	1.03	1.04	1.29	1.18	0.66	0.96	1.46	1.11	0.89
We1	1.67	0.98	1.23	0.82	2.69	1.73	1.81	0.45	0.43	1.11	1.60	0.92	0.70
We2	1.02	0.56	1.19	0.26	0.90	0.84	1.39	0.38	0.30	0.47	0.70	0.77	0.36
We3	1.07	0.81	0.49	1.40	1.46	1.34	2.36	0.60	0.74	1.28	2.35	1.80	0.60
We4	1.34	1.80	1.64	1.52	1.72	1.81	3.77	2.87	1.24	1.33	5.76	3.16	1.11
We5	1.54	2.25	1.71	1.83	2.84	1.02	2.46	1.99	0.76	1.52	2.46	2.07	1.67
We6	2.39	2.42	2.44	2.29	3.76	2.41	3.21	1.60	0.94	1.85	3.05	2.36	2.49
Wi1	0.32	0.26	0.26	0.16	0.52	0.21	0.47	0.16	0.20	0.13	0.17	0.15	0.07
Wi2	0.22	0.21	0.26	0.11	0.21	0.35	0.49	0.15	0.09	0.13	0.17	0.17	0.07
Wi3	0.23	0.42	0.49	0.10	0.30	0.28	0.26	0.20	0.14	0.22	0.22	0.17	0.13
Wi4	0.33	0.47	0.34	0.29	0.30	0.46	0.22	0.16	0.23	0.34	0.39	0.19	0.34
Wi5	0.25	0.38	0.24	0.31	0.23	0.35	0.46	0.15	0.32	0.30	0.43	0.19	0.29

Table 19: Electric conductivity at sampling points

sample point ID	Dec-03 µS/cm	Apr-04 µS/cm	Jun-04 µS/cm	Oct-04 µS/cm	Dec-04 µS/cm	Apr-05 µS/cm	Jun-05 µS/cm	Sep-05 µS/cm	Dec-05 µS/cm	Mar-06 µS/cm	Jun-06 µS/cm	Sep-06 µS/cm
La1	1766	1367	1316	911	1451	1104	1482	1500	1296	1726	1613	1309
La2	.	.	1070	1519	1496	1112	1564	1401	1255	1327	1307	1262
Mo1	516	458	467	412	462	408	492	506	489	440	443	477
Mo2	958	873	722	878	861	636	852	1036	811	740	799	900
Mo3	891	713	734	841	864	562	748	948	860	694	794	738
Mo4	976	897	760	923	930	647	829	936	1037	751	696	823
Sa1	847	668	677	743	730	556	700	832	833	619	705	721
Sa2	837	769	672	821	782	586	759	856	866	620	713	487
Sa3	827	736	696	778	786	605	754	844	888	665	700	380
Sw1	716	703	707	707	823	626	726	710	741	702	745	779
Sw2	966	857	864	773	866	722	783	938	871	810	800	879
Sw3	1385	1152	982	1218	1239	908	1185	1270	1097	1010	1007	1162
Sw3b	924	864	877	893	915	682	926	924	882	775	815	891
Sw4	965	851	835	857	924	679	912	924	887	794	840	875
Sw5	1299	1195	913	1189	1316	805	1302	1009	1121	953	896	1059
We1	507	365	447	311	397	301	421	490	481	366	353	400
We2	474	354	427	399	411	288	400	480	447	384	340	395
We3	821	1195	1086	922	1041	766	749	717	748	713	896	850
We4	822	685	718	632	624	637	624	866	575	641	505	686
We5	936	702	738	750	740	463	551	925	557	660	544	737
We6	872	717	785	764	814	545	577	954	544	699	567	721
Wi1	450	413	434	275	416	361	422	529	473	391	398	425
Wi2	472	419	438	445	434	369	449	430	536	420	424	443
Wi3	493	472	437	457	446	370	400	425	557	406	413	380
Wi4	783	686	769	838	766	493	692	805	745	776	682	721
Wi5	796	730	755	858	790	505	740	825	728	774	679	748

Table 20: BPA concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	1662	< LOD	< LOD	< LOD	567	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	86
La2	.	.	.	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	130	65	< LOD	107
Mo1	.	< LOD	< LOD	< LOD	381	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Mo2	983	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	58
Mo3	< LOD	< LOD	< LOD	< LOD	81	< LOD	< LOD	< LOD	< LOD	73	< LOD	< LOD	121
Mo4	1547	< LOD	< LOD	< LOD	74	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	118
Sa1	1924	< LOD	< LOD	< LOD	83	< LOD	< LOD	< LOD	< LOD	66	.	< LOD	96
Sa2	< LOD	< LOD	< LOD	< LOD	119	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	633
Sa3	< LOD	< LOD	< LOD	< LOD	107	< LOD	< LOD	< LOD	< LOD	152	< LOD	< LOD	894
Sw1	< LOD	< LOD	< LOD	< LOD	.	< LOD	< LOD	< LOD	< LOD	179	< LOD	< LOD	< LOD
Sw2	< LOD	< LOD	< LOD	< LOD	86	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOQ
Sw3	< LOD	< LOD	122	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sw3b	< LOD	< LOD	< LOD	< LOD	56	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sw4	1324	< LOD	139	.	< LOD	< LOD	< LOD	< LOD	< LOD	99	< LOD	< LOD	< LOD
Sw5	< LOD	< LOD	< LOD	< LOD	22	330	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ
We1	< LOD	< LOD	< LOD	< LOD	69	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD
We2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
We3	< LOD	< LOD	< LOD	< LOD	80	88	< LOD	< LOD	< LOD	94	< LOD	< LOQ	74
We4	.	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ	< LOQ
We5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ	< LOQ
We6	229	< LOD	< LOD	< LOD	57	< LOD	< LOD	< LOD	< LOD	56	< LOD	< LOQ	< LOD
Wi1	< LOD	< LOD	< LOD	< LOD	125	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi3	< LOD	< LOD	< LOD	< LOD	23	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ
Wi4	< LOD	< LOD	< LOD	< LOD	1139	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	146
Wi5	< LOD	< LOD	< LOD	< LOD	1497	< LOD	< LOD	< LOD	< LOD	122	128	< LOD	86

Table 21: OP concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	100	< LOD	40	104	< LOD	< LOD	< LOD	228	< LOD	< LOD	478	< LOD	48
La2	.	.	.	47	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	60	< LOD	< LOQ
Mo1	.	< LOD	< LOD	< LOD	96	< LOQ	30	< LOQ	40	< LOD	< LOQ	< LOQ	31
Mo2	156	34	< LOQ	< LOQ	73	67	< LOD	< LOD	< LOD	< LOQ	30	< LOD	< LOQ
Mo3	118	40	35	42	114	39	< LOD	< LOD	< LOD	38	35	< LOD	41
Mo4	83	54	< LOQ	< LOQ	92	36	< LOD	< LOD	32	< LOD	< LOQ	< LOD	43
Sa1	145	33	< LOQ	31	102	32	< LOD	43	44	< LOQ	.	< LOD	< LOQ
Sa2	127	32	< LOQ	< LOQ	150	33	< LOD	46	< LOD	< LOQ	46	< LOD	32
Sa3	117	< LOQ	< LOQ	31	64	50	< LOD	< LOD	38	41	36	< LOD	< LOQ
Sw1	60	< LOQ	< LOQ	< LOD	.	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOD
Sw2	48	50	58	< LOD	41	57	< LOD	45	46	< LOQ	< LOQ	< LOD	33
Sw3	142	79	29	< LOQ	48	53	< LOD	< LOD	62	< LOD	38	< LOD	41
Sw3b	65	79	41	< LOD	39	40	< LOD	< LOD	36	< LOD	32	< LOD	< LOQ
Sw4	83	41	61	.	41	50	< LOD	< LOD	< LOQ	< LOD	34	< LOD	< LOQ
Sw5	86	70	35	.	34	41	< LOD	< LOD	87	< LOD	43	< LOD	36
We1	30	< LOQ	< LOD	< LOD	32	< LOQ	< LOD	< LOQ	< LOD	< LOQ	50	< LOQ	< LOD
We2	45	< LOD	93	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOQ	< LOD
We3	153	56	273	112	148	257	131	112	< LOQ	66	180	253	32
We4	.	70	34	32	38	86	< LOD	91	< LOQ	< LOQ	81	95	< LOQ
We5	420	108	56	< LOQ	55	84	< LOD	79	< LOD	37	85	86	< LOQ
We6	45	51	70	< LOQ	50	96	< LOD	96	< LOQ	33	91	89	32
Wi1	48	< LOD	< LOD	< LOD	49	48	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOD
Wi2	78	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOQ	< LOQ	< LOQ	< LOD
Wi3	32	< LOD	< LOQ	32	< LOQ	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD
Wi4	< LOD	50	< LOQ	< LOQ	39	39	< LOD	< LOQ	< LOQ	< LOQ	58	< LOD	< LOQ
Wi5	50	36	< LOQ	53	37	< LOQ	< LOD	< LOQ	< LOQ	< LOQ	66	55	< LOQ

Table 22: NP concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	225	47	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
La2	.	.	.	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOQ	< LOD
Mo1	.	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	122	31	33	60	.
Mo2	442	< LOQ	38	< LOQ	< LOD	37	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOQ
Mo3	526	25	< LOD	< LOD	48	38	< LOD	< LOD	< LOQ	43	33	< LOD	< LOQ
Mo4	644	< LOQ	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOD	65	< LOQ
Sa1	597	48	< LOD	< LOD	26	32	< LOD	< LOD	44	< LOQ	.	54	< LOD
Sa2	622	192	< LOD	< LOD	44	< LOQ	< LOD	< LOD	42	32	31	112	114
Sa3	723	42	< LOD	< LOQ	57	< LOQ	< LOD	< LOD	90	45	27	35	< LOQ
Sw1	770	< LOQ	< LOD	< LOD	.	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD	34	< LOD
Sw2	208	83	33	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	58	< LOQ	43	< LOQ
Sw3	426	104	30	< LOD	< LOD	< LOD	< LOD	< LOD	65	< LOQ	< LOQ	57	< LOD
Sw3b	401	170	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOQ	26	< LOQ	< LOQ	< LOQ
Sw4	397	71	< LOQ	.	< LOD	< LOD	< LOD	< LOD	36	< LOQ	< LOQ	< LOQ	< LOQ
Sw5	361	69	27	< LOD	< LOD	< LOQ	< LOD	< LOD	89	< LOQ	40	30	29
We1	57	< LOQ	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOQ	51	37	28	< LOQ
We2	403	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	61	47	86	< LOD
We3	261	< LOQ	< LOQ	< LOQ	< LOD	< LOQ	< LOD	< LOD	< LOD	67	61	52	< LOQ
We4	.	53	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	36	63	< LOQ	37	< LOD
We5	717	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	37	67	30	54	< LOQ
We6	270	< LOD	< LOQ	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	82	33	75	< LOQ
Wi1	554	< LOD	< LOQ	< LOD	< LOQ	< LOQ	< LOD	< LOD	31	87	< LOQ	54	< LOD
Wi2	516	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	42	32	<LOQ	37	< LOD
Wi3	618	< LOD	< LOD	< LOD	< LOD	26	< LOD	< LOD	< LOD	82	< LOQ	< LOQ	36
Wi4	33	120	< LOD	32	< LOD	< LOQ	< LOD	< LOD	27	98	76	< LOQ	< LOQ
Wi5	184	73	< LOQ	< LOD	< LOD	< LOQ	< LOD	< LOD	34	82	< LOD	< LOQ	< LOD

Table 23: HHCB concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	125	417	411	389	678	592	412	616	313	320	840	169	295
La2	.	.		97	308	385	347	101	104	224	233	100	90
Mo1	.	< LOQ	< LOQ	< LOD	113	19	< LOQ	20	28	21	30	18	25
Mo2	< LOD	340	233	142	384	460	206	167	191	66	233	121	147
Mo3	104	268	137	109	314	144	156	122	105	104	192	78	141
Mo4	59	306	153	72	379	178	205	92	67	176	98	77	112
Sa1	< LOD	163	107	77	195	121	136	121	114	103	.	68	74
Sa2	83	80	65	68	413	119	131	92	101	74	107	68	59
Sa3	< LOD	134	59	57	165	170	121	78	74	90	90	68	93
Sw1	< LOQ	< LOQ	< LOQ	< LOD	.	< LOQ	18	< LOQ	< LOD	< LOQ	< LOQ	25	< LOD
Sw2	< LOD	367	194	177	322	246	274	243	237	163	254	124	188
Sw3	< LOD	316	167	90	210	250	254	145	127	184	217	118	161
Sw3b	< LOD	141	148	123	175	233	249	223	90	220	188	116	108
Sw4	100	155	202	.	197	266	204	201	113	188	167	118	73
Sw5	102	289	230	101	203	342	266	92	159	260	181	84	58
We1	112	65	38	55	193	58	45	86	50	29	.	< LOQ	68
We2	43	29	22	32	29	50	39	38	34	35	55	< LOQ	37
We3	168	132	252	217	296	274	190	248	94	117	201	104	162
We4	.	155	81	131	130	118	133	219	95	73	135	33	75
We5	104	137	122	76	179	109	89	186	87	75	123	41	99
We6	58	105	147	63	178	143	127	123	65	77	132	36	136
Wi1	< LOQ	< LOD	< LOQ	< LOD	49	26	< LOQ	< LOQ	< LOD	< LOD	.	< LOD	< LOD
Wi2	20	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOD	< LOD	< LOQ	< LOD	< LOD
Wi3	53	< LOD	41	163	< LOD	< LOQ	< LOQ	< LOD	< LOD	< LOD	.	< LOQ	< LOQ
Wi4	72	105	93	55	135	155	140	48	69	86	171	58	131
Wi5	66	130	112	187	122	145	134	32	70	62	173	31	54

Table 24: AHTN concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	86	159	144	132	299	227	170	223	79	49	135	55	118
La2	.	.	.	.	98	123	93	27	24	32	36	< LOQ	32
Mo1	.	< LOQ	< LOD	< LOD	38	19	< LOD	< LOQ	< LOQ	< LOD	< LOQ	< LOD	17
Mo2	< LOD	133	69	46	119	137	43	44	32	< LOQ	34	21	46
Mo3	20	96	41	33	91	44	31	25	20	< LOQ	27	< LOQ	44
Mo4	< LOD	97	50	27	126	51	37	23	< LOQ	24	< LOQ	< LOQ	38
Sa1	< LOD	54	34	25	62	36	30	28	21	< LOQ	.	< LOQ	26
Sa2	40	24	21	25	120	35	29	24	19	< LOQ	19	< LOQ	23
Sa3	< LOD	41	20	20	50	47	27	22	< LOQ	< LOQ	< LOQ	< LOQ	33
Sw1	< LOD	< LOD	< LOQ	< LOD	.	< LOD	< LOQ	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD
Sw2	< LOD	103	72	61	102	70	68	67	47	23	38	26	58
Sw3	< LOD	97	57	32	70	74	61	39	30	24	33	19	54
Sw3b	< LOD	50	55	46	65	71	60	58	20	31	28	19	34
Sw4	68	56	75	.	67	83	46	51	24	26	25	19	22
Sw5	73	90	78	41	73	102	65	25	36	36	28	< LOQ	20
We1	< LOD	26	< LOQ	20	66	19	< LOQ	24	< LOQ	< LOD	< LOQ	< LOQ	21
We2	22	< LOQ	< LOQ	< LOQ	2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
We3	< LOD	47	77	63	96	82	42	51	19	18	28	20	45
We4	.	55	28	36	44	39	31	40	19	< LOQ	22	< LOQ	22
We5	46	49	41	21	60	34	22	35	17	< LOQ	19	< LOQ	30
We6	< LOD	39	45	< LOQ	50	42	31	29	< LOQ	< LOQ	19	< LOQ	38
Wi1	< LOQ	< LOD	< LOD	< LOD	22	27	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi2	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi3	32	< LOD	< LOQ	65	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi4	< LOD	41	32	73	53	53	27	< LOQ	< LOQ	< LOQ	25	< LOQ	55
Wi5	46	54	37	20	45	47	29	< LOQ	< LOQ	< LOQ	25	< LOQ	22

Table 25: TCPP concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	252	647	624	972	1307	1046	1309	2278	1547	473	1891	1501	1020
La2	.	.	.	897	1441	959	1263	1909	1611	592	666	1242	1144
Mo1	.	27	18	61	162	43	55	298	462	37	30	61	280
Mo2	315	499	410	559	910	1095	629	1716	1207	178	460	1042	875
Mo3	518	408	217	560	1170	410	216	1202	1314	286	413	997	790
Mo4	458	629	1082	746	1662	614	592	1347	1370	535	291	1294	344
Sa1	281	452	195	275	651	229	182	821	1123	255	.	803	492
Sa2	406	349	315	449	1630	378	321	1092	1164	304	207	785	479
Sa3	463	328	283	497	758	541	456	948	1168	478	260	933	517
Sw1	89	40	89	102	.	98	95	863	63	108	66	1982	56
Sw2	521	786	506	1053	1235	735	1016	1672	2819	540	441	1148	1044
Sw3	562	706	499	779	1175	745	963	1604	2474	562	546	1168	2840
Sw3b	541	675	449	910	1005	600	950	1879	1680	542	343	1068	3427
Sw4	587	566	612	.	928	781	825	1581	2177	482	314	1175	1625
Sw5	479	671	504	1014	1287	1241	954	1449	3846	676	1192	1122	1021
We1	444	225	78	248	369	124	108	345	383	44	71	139	258
We2	317	112	206	239	177	133	34	173	519	56	94	130	207
We3	623	325	545	894	814	456	453	1047	2028	334	314	960	664
We4	.	465	223	498	394	242	327	928	1631	163	499	311	453
We5	815	505	224	355	550	280	218	1124	1052	158	257	388	609
We6	391	417	297	386	643	373	317	921	1776	154	209	412	990
Wi1	93	12	14	< LOD	142	175	17	39	15	13	13	20	13
Wi2	128	< LOD	< LOQ	158	23	15	13	35	34	11	< LOQ	< LOQ	20
Wi3	349	< LOQ	128	1639	20	14	11	50	28	< LOQ	< LOD	35	134
Wi4	394	316	231	802	723	352	382	625	984	163	312	713	1349
Wi5	333	290	253	2914	720	324	482	718	986	160	308	675	764

Table 26: TDCPP concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	32	81	61	168	153	76	1199	341	113	123	153	266	94
La2	.	.	.	206	103	91	1284	227	148	52	103	291	110
Mo1	.	31	< LOQ	55	119	13	52	27	75	21	13	40	70
Mo2	163	163	51	200	115	112	236	147	203	38	69	253	96
Mo3	121	142	39	234	153	47	91	111	230	69	72	245	114
Mo4	54	183	64	37	151	65	190	166	170	87	42	187	102
Sa1	136	98	34	224	92	30	149	137	146	64	.	152	77
Sa2	80	88	39	303	231	45	141	155	204	62	51	153	73
Sa3	< LOD	90	43	252	107	83	186	158	167	71	60	< LOD	71
Sw1	33	14	20	14	.	14	57	132	16	17	14	46	8
Sw2	138	119	78	113	171	68	390	302	349	138	85	259	105
Sw3	80	100	66	148	112	78	825	278	317	139	96	293	166
Sw3b	123	119	70	71	136	60	406	388	289	145	72	263	147
Sw4	143	105	102	.	137	82	327	341	307	132	62	266	98
Sw5	106	98	73	46	125	102	758	278	534	192	80	292	101
We1	95	107	30	211	140	40	59	122	104	32	< LOD	67	83
We2	114	62	136	65	37	41	16	54	100	40	40	77	65
We3	79	58	52	653	128	45	209	166	118	82	72	234	76
We4	.	74	34	101	86	37	140	202	99	62	59	130	74
We5	72	68	40	57	102	37	88	206	93	64	73	160	89
We6	59	64	48	71	100	35	149	229	132	69	47	164	132
Wi1	31	< LOQ	< LOQ	< LOD	73	20	31	< LOD	< LOD	< LOQ	< LOD	< LOQ	< LOQ
Wi2	85	< LOQ	< LOD	< LOQ	< LOQ	< LOQ	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ
Wi3	101	< LOD	17	112	< LOQ	< LOD	32	< LOD	11	< LOQ	< LOD	12	27
Wi4	59	48	31	144	124	39	136	83	119	56	47	143	136
Wi5	88	42	34	333	126	42	210	98	133	61	59	145	82

Table 27: TCEP concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	145	84	166	339	352	200	209	927	554	348	463	513	327
La2	.	.	.	424	289	176	249	536	695	319	281	565	345
Mo1	.	< LOD	< LOD	46	68	< LOQ	< LOQ	82	77	< LOQ	< LOQ	20	.
Mo2	248	149	97	165	228	359	153	697	601	107	1190	356	256
Mo3	294	93	47	123	286	94	69	462	557	130	978	334	309
Mo4	< LOD	159	110	154	373	130	86	599	606	247	378	319	310
Sa1	231	82	68	46	150	41	84	383	396	101	.	196	207
Sa2	176	81	106	< LOD	417	58	81	542	390	112	564	186	684
Sa3	557	72	52	82	199	104	110	470	436	235	754	267	397
Sw1	< LOD	12	72	33	.	29	14	264	26	34	18	531	29
Sw2	339	170	142	300	314	161	144	780	1067	277	153	478	305
Sw3	319	90	178	326	243	159	165	650	997	311	210	471	592
Sw3b	240	162	122	210	243	147	125	837	718	338	135	399	521
Sw4	316	114	151	.	227	175	108	781	807	311	114	453	329
Sw5	247	126	180	494	279	200	182	516	2019	327	161	442	317
We1	< LOD	32	27	26	67	18	< LOQ	170	88	21	30	39	117
We2	218	18	175	26	27	23	< LOD	88	117	25	42	42	95
We3	139	32	125	90	140	62	47	359	116	89	180	253	217
We4	.	42	166	71	73	36	36	457	148	57	133	108	158
We5	196	61	63	52	104	47	16	457	157	59	136	132	205
We6	72	57	86	67	124	53	27	464	234	62	101	140	251
Wi1	< LOD	< LOD	23	< LOD	60	53	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD	< LOQ
Wi2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOQ	< LOD	< LOQ
Wi3	125	< LOD	37	116	< LOQ	< LOD	< LOD	28	< LOQ	< LOQ	< LOQ	16	80
Wi4	< LOD	44	60	108	135	51	35	185	323	90	158	202	561
Wi5	155	37	69	236	142	58	55	236	280	80	155	185	323

Table 28: DEET concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	118	135	146	253	< LOD	143	289	911	563	404	587	202	275
La2	.	.	.	503	< LOD	122	327	644	637	645	146	154	274
Mo1	.	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	.
Mo2	93	102	41	133	< LOD	39	48	249	< LOD	< LOD	27	124	127
Mo3	166	100	26	151	216	< LOQ	95	936	< LOD	< LOD	39	96	127
Mo4	82	133	46	116	187	93	83	428	< LOD	106	121	120	159
Sa1	101	110	23	99	< LOD	< LOQ	37	272	< LOD	< LOD	.	86	67
Sa2	123	117	30	74	< LOD	< LOQ	46	285	< LOD	< LOD	< LOQ	66	55
Sa3	82	134	27	143	< LOD	< LOD	65	268	< LOD	27	28	84	67
Sw1	< LOD	< LOD	< LOD	< LOQ	.	< LOQ	< LOQ	268	< LOD	< LOD	< LOQ	28	< LOD
Sw2	135	64	62	173	< LOD	118	165	417	895	471	161	200	206
Sw3	112	169	67	246	< LOD	101	197	519	717	535	170	163	366
Sw3b	110	64	56	1292	< LOD	< LOD	142	529	389	458	163	192	165
Sw4	146	32	68	.	< LOD	106	125	447	713	62< LOD	112	203	121
Sw5	130	97	57	392	430	71	152	392	1142	377	133	165	226
We1	< LOD	89	< LOD	24	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	38	40
We2	85	66	35	39	< LOD	14	< LOD	< LOD	< LOD	< LOD	24	29	34
We3	106	72	< LOD	63	< LOD	62	52	347	< LOD	< LOD	121	328	149
We4	.	101	< LOQ	55	< LOD	< LOQ	56	252	< LOD	< LOD	76	134	77
We5	380	114	< LOQ	41	< LOD	27	36	209	< LOD	< LOD	71	215	108
We6	95	93	< LOQ	50	56	36	33	239	< LOD	< LOD	74	246	168
Wi1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD
Wi2	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD
Wi3	127	< LOD	31	166	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ
Wi4	< LOD	51	66	115	538	41	44	274	< LOD	< LOD	164	163	325
Wi5	78	49	73	272	484	39	564	308	< LOD	< LOD	167	152	156

Table 29: Terbutryn concentrations

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	111	68	41	90	122	45	139	69	< LOD	37	< LOD	63	90
La2	.	.	.	106	127	34	147	143	< LOD	45	19	64	69
Mo1	.	< LOD	< LOD	< LOD	200	< LOD	51	19	66	< LOD	< LOD	< LOD	.
Mo2	492	252	446	711	1455	761	438	1504	620	210	314	402	658
Mo3	< LOD	323	536	655	2225	291	394	1907	965	428	196	371	1028
Mo4	594	193	374	304	1401	213	242	1172	754	264	117	261	984
Sa1	332	308	648	808	2169	436	561	1260	1304	483	.	335	901
Sa2	384	284	441	593	3067	313	537	1326	1252	347	288	382	420
Sa3	< LOD	258	331	651	1231	370	622	1103	1222	371	283	377	494
Sw1	15	< LOD	< LOD	< LOD	.	< LOD	13	104	< LOD	< LOD	< LOD	< LOD	< LOD
Sw2	129	19	14	172	106	< LOD	76	182	246	37	< LOD	41	59
Sw3	142	31	34	88	86	22	99	139	< LOD	38	< LOD	56	120
Sw3b	109	14	< LOD	99	77	< LOD	69	173	162	41	< LOD	35	75
Sw4	140	14	15	.	82	13	58	149	189	35	< LOD	36	41
Sw5	111	168	24	133	65	31	90	118	< LOD	36	< LOD	45	64
We1	< LOD	< LOD	< LOD	< LOD	46	< LOD	< LOD	43	19	< LOD	< LOD	< LOD	13
We2	132	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	27	27	< LOD	< LOD	< LOD	< LOD
We3	559	318	286	5600	1698	649	459	937	447	1572	939	367	1552
We4	.	372	54	2098	807	215	243	762	529	650	659	104	1039
We5	516	531	109	1652	991	287	106	727	483	982	576	173	1418
We6	222	388	117	1505	1408	275	261	733	602	1024	501	169	2277
Wi1	19	< LOD	< LOD	< LOD	73	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	61
Wi2	29	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi3	42	< LOD	28	37	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wi4	< LOD	22	66	< LOD	63	16	22	104	56	< LOD	< LOD	21	110
Wi5	51	< LOD	70	81	554	14	30	105	57	< LOD	< LOD	22	57

Table 30: TBEP concentration

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	188	1233	143	336	645	731	253	118	< LOD	< LOD	385	191	398
La2	.	.	.	316	559	759	248	389	< LOD	305	190	206	177
Mo1	.	38	36	106	< LOD	260	155	88	60	62	238	71	< LOD
Mo2	480	187	164	212	365	512	134	< LOD	72	72	211	< LOD	75
Mo3	726	116	165	166	399	145	103	< LOD	144	224	191	< LOD	208
Mo4	223	163	115	124	278	331	223	256	135	362	170	< LOD	202
Sa1	739	290	197	138	232	191	121	169	123	221	.	398	< LOD
Sa2	711	142	127	118	452	274	190	221	149	168	165	142	912
Sa3	3889	172	129	177	238	289	195	248	137	207	199	170	1328
Sw1	185	49	52	65	.	77	53	983	12	87	156	< LOD	< LOD
Sw2	197	2204	940	375	250	265	197	444	520	217	351	< LOD	314
Sw3	210	689	285	194	390	421	199	413	133	206	385	621	234
Sw3b	148	541	326	166	294	410	252	613	335	< LOD	381	224	197
Sw4	179	631	455	.	244	299	170	480	369	< LOD	285	255	100
Sw5	229	384	271	279	219	378	208	406	261	191	345	131	319
We1	160	53	134	25	< LOD	285	82	129	46	32	241	52	< LOD
We2	124	42	440	28	43	117	45	49	54	42	253	86	58
We3	78	172	136	123	156	298	164	228	506	62	218	136	47
We4	.	318	109	62	197	349	210	275	241	44	532	105	123
We5	256	260	208	52	160	252	273	461	201	54	428	105	129
We6	117	208	103	121	133	269	198	492	208	59	263	96	151
Wi1	158	25	254	< LOD	< LOD	624	68	11	17	28	73	74	17
Wi2	264	< LOD	158	25	33	325	160	26	22	31	99	43	23
Wi3	113	20	326	46	49	157	42	27	23	36	68	42	100
Wi4	395	152	135	76	45	330	52	68	181	287	763	189	15
Wi5	104	106	138	112	< LOD	203	150	57	39	< LOD	720	142	69

Table 31: TBP concentrations at sampling points

ID	Sep-03	Dec-03	Apr-04	Jun-04	Oct-04	Dec-04	Apr-05	Jun-05	Sep-05	Dec-05	Mar-06	Jun-06	Sep-06
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
La1	188	1233	143	336	645	731	253	880	329	90	1096	62	145
La2	.	.	.	316	559	759	248	506	237	141	304	278	81
Mo1	.	38	36	106	< LOD	260	155	393	333	33	93	164	441
Mo2	480	187	164	212	365	512	134	273	118	26	137	172	109
Mo3	726	116	165	166	399	145	103	301	184	65	90	179	175
Mo4	223	163	115	124	278	331	223	265	213	104	56	169	180
Sa1	739	290	197	138	232	191	121	262	167	48	.	171	94
Sa2	711	142	127	118	452	274	190	296	213	54	116	202	257
Sa3	3889	172	129	177	238	289	195	351	170	90	243	184	213
Sw1	185	49	52	65	.	77	53	223	197	42	36	58	55
Sw2	197	2204	940	375	250	265	197	403	268	66	80	174	124
Sw3	210	689	285	194	390	421	199	359	275	107	142	275	190
Sw3b	148	541	326	166	294	410	252	477	219	102	81	83	231
Sw4	179	631	455	.	244	299	170	442	215	82	75	107	108
Sw5	229	384	271	279	219	378	208	425	511	124	135	273	112
We1	160	53	134	25	< LOD	285	82	376	113	17	96	52	68
We2	124	42	440	28	43	117	45	224	86	24	47	66	58
We3	78	172	136	123	156	298	164	266	< LOD	67	195	126	76
We4	.	318	109	62	197	349	210	189	111	39	117	55	58
We5	256	260	208	52	160	252	273	204	344	51	150	73	85
We6	117	208	103	121	133	269	198	232	584	51	110	67	129
Wi1	158	25	254	< LOD	< LOD	624	68	41	54	21	36	44	< LOQ
Wi2	264	< LOD	158	25	33	325	160	350	222	83	33	42	< LOQ
Wi3	113	20	326	46	49	157	42	97	14	28	101	< LOQ	76
Wi4	395	152	135	76	45	330	52	124	49	96	137	65	121
Wi5	104	106	138	112	< LOD	203	150	116	64	33	133	59	32

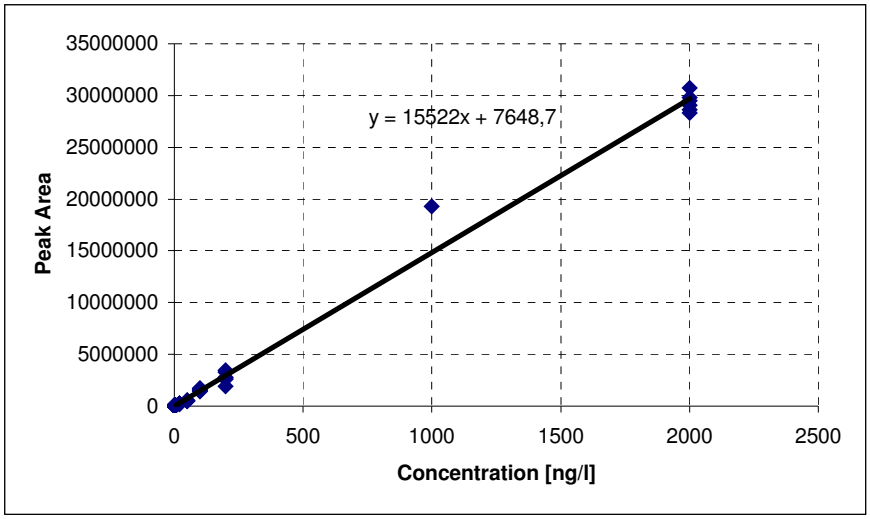

Figure 25: Calibration line of HHCB

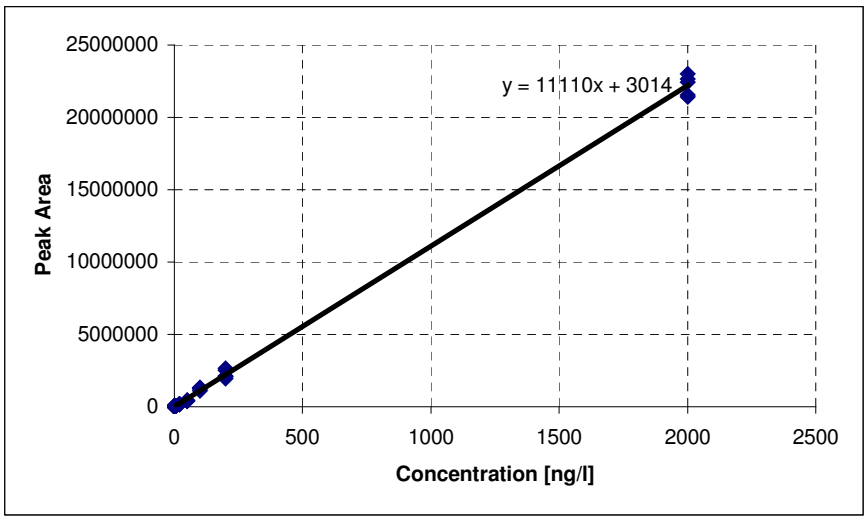

Figure 26: Calibration line of AHTN

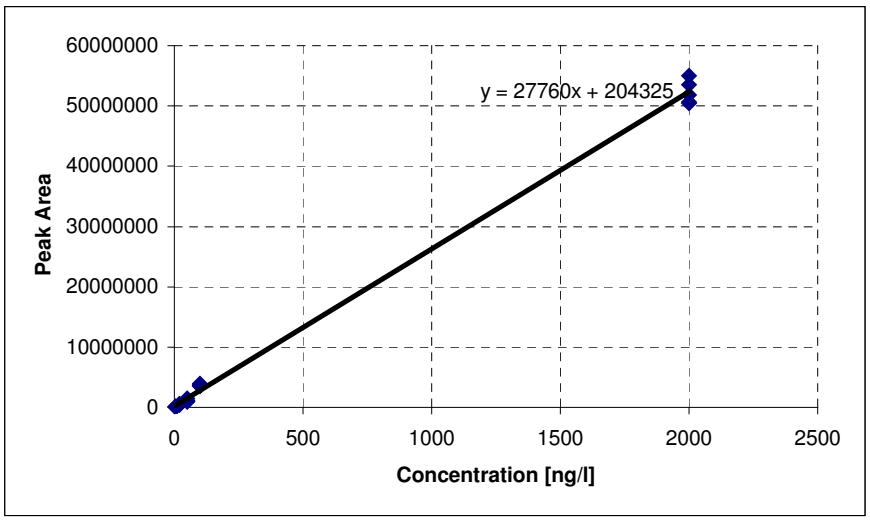

Figure 27: Calibration line of DEET

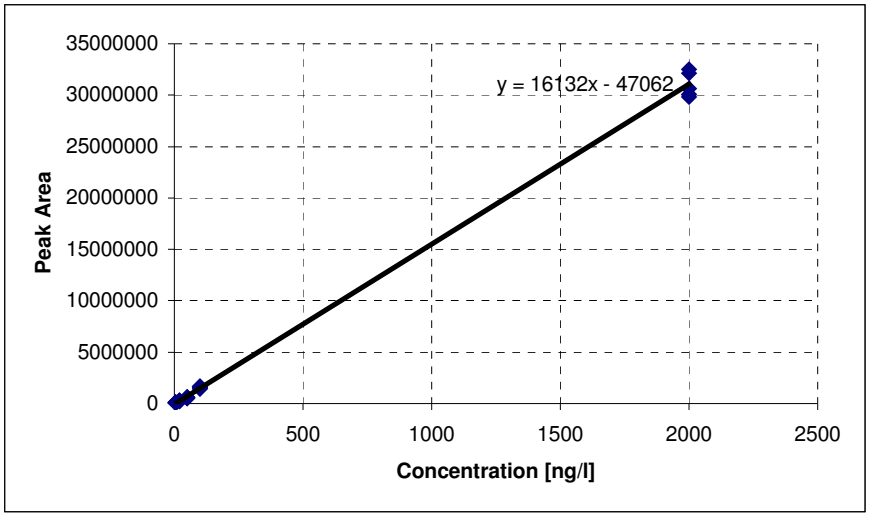

Figure 28: Calibration line of TCPP

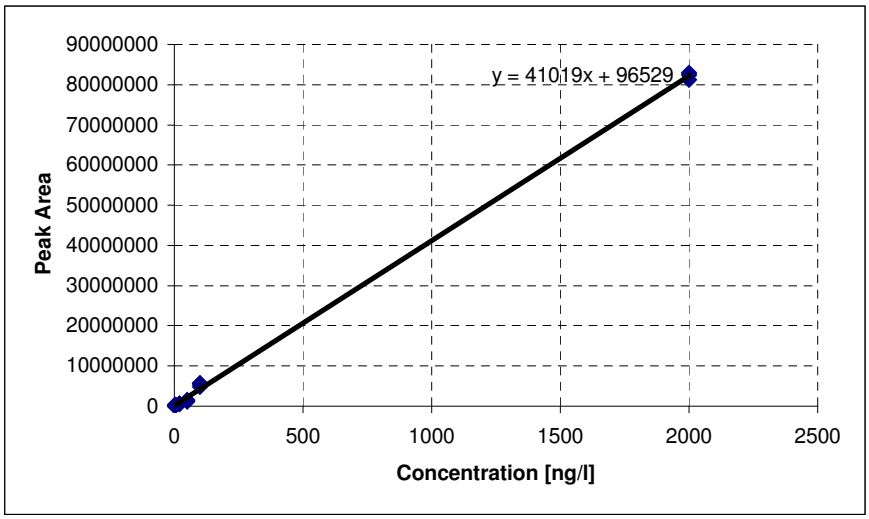

Figure 29: Calibration line of TCEP

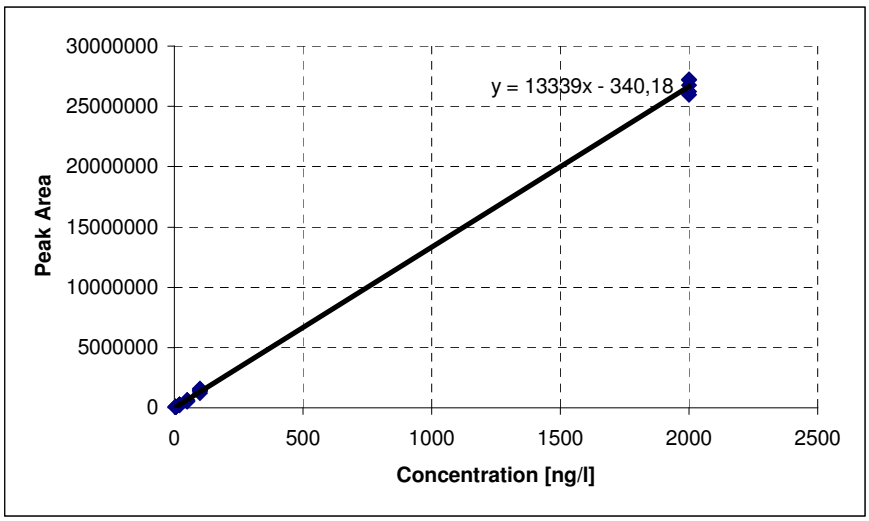

Figure 30: Calibration line of TDCPP

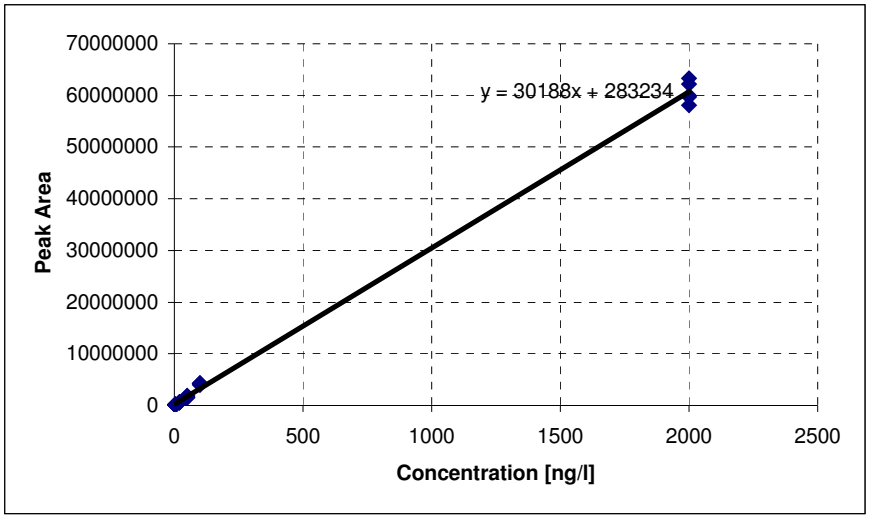

Figure 31: Calibration line of TBP

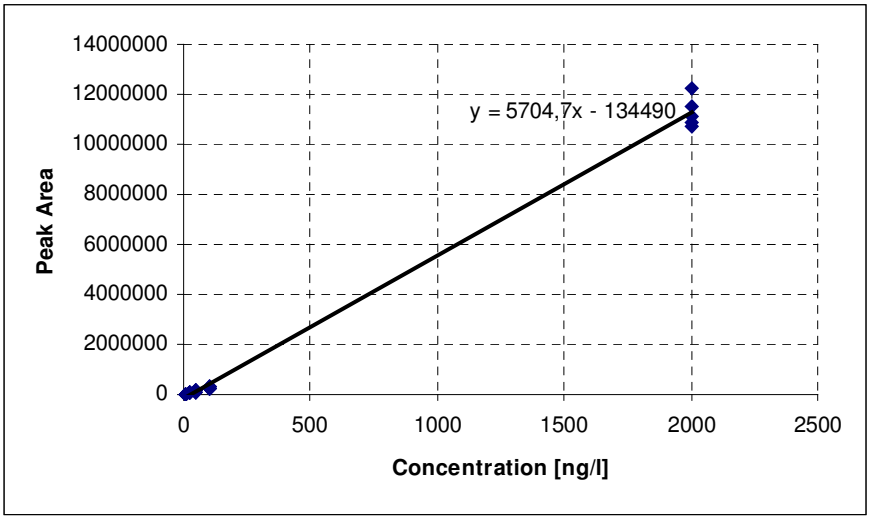

Figure 32: Calibration line of TBEP

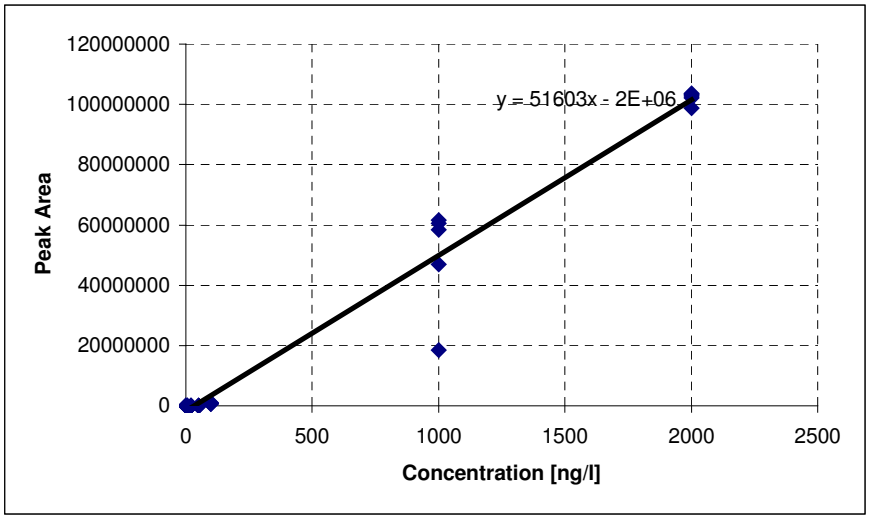

Figure 33: Calibration line of BPA

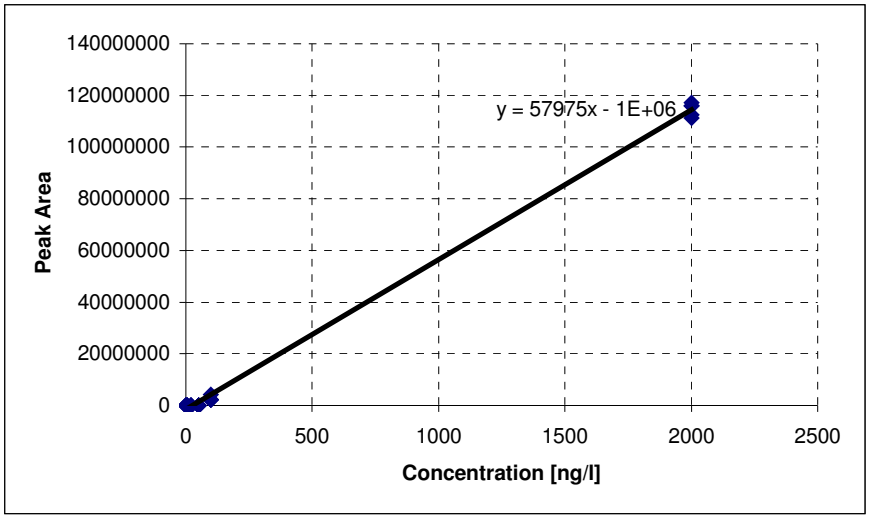

Figure 34: Calibration line of NP

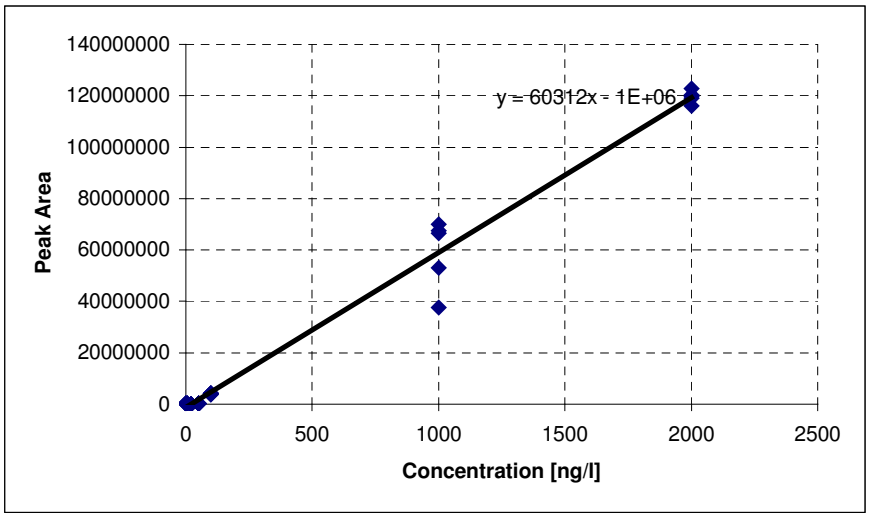

Figure 35: Calibration line of OP

CURRICULUM VITAE

Persönliche Daten

Name	Kristin Quednow
Geburtsdatum	22.05.1975
Geburtsort	Rüdersdorf bei Berlin
Staatsangehörigkeit	deutsch

Berufspraxis

08/2003 – 12/2007	Wissenschaftliche Mitarbeiterin am Institut für Atmosphäre und Umwelt in der Abteilung Umweltanalytik der Johann-Wolfgang-von-Goethe-Universität Frankfurt am Main

Praktika & sonst. Tätigkeiten

03/1998 - 05/1998	Fachpraktikum, Ingenieurbüro Dr. Fechter GmbH, Berlin
09/1996 - 12/1996	Lehrstuhl Aufbereitungstechnik BTU Cottbus, Arbeit als Studentische Hilfskraft
08/1995	Grundpraktikum, Umweltamt Berlin-Köpenick

Studium & Auslandsaufenthalt

10/1994 - 12/2002	Studium des Umweltingenieurwesens an der Technischen Universität Cottbus, Schwerpunkte: Wasser- und Abwassertechnik, Hydrologie, Gewässerschutz, Bodenkunde, Altlasten, Rekultivierung Thema der Diplomarbeit: „Kohlenstoffvorräte im Boden und der Vegetation bei verschiedenen Landnutzungen in einer ländlichen Region Mexikos“
02/2000 - 12/2000	Auslandsaufenthalt in Mexiko am Colegio de Postgraduados Texcoco, Praktikum und Datensammlung für Diplomarbeit Mitarbeit am "Oaxaca Sustainable Hillside Management Project"

Schulausbildung

1989 - 1994	Heinrich-Schliemann-Gymnasium, Berlin
1981 - 1989	Polytechnische Oberschule Berlin-Wilhelmshagen